Systematic Survey on Petrochemical Technology

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Keizo Tajima

■ Abstract

The petrochemical industry involves the production of basic petrochemicals, industrial organic chemicals and polymers using petroleum or natural gas as the raw material. The industry took hold in Japan in the 1950s and almost immediately dominated the chemical industry; to this day, the petrochemical industry still remains a key industry, providing raw materials to a wide range of sectors in the Japanese chemical industry, including pharmaceuticals, cosmetics, synthetic detergents, paints, plastic molding and rubber molding. By the 1960s, a mass supply of plastic products had dramatically impacted society, triggering a polymer revolution and undergirding Japan’s rapid economic growth. New chemical factory conglomerates sprang up along the coastlines, known as petrochemical industrial complexes or *kombinats*.

The petrochemical industry originated in the 1920s in the United States. However, up until the early 1940s, it was little more than a chemical industry that existed only in the United States, supplying a few industrial organic chemicals. Wood chemistry, oleochemistry, fermentation chemistry and coal chemistry had all long flourished to the point of mass production prior to the advent of petrochemistry, in Europe, the United States and Japan alike. Petrochemistry co-existed with these in the United States as yet another type of chemical industry. The development of naphtha steam-cracking technology in the 1940s and the European migration of the petrochemical industry in the 1950s had a major impact on petrochemical technology. Innovations in petrochemical technology suddenly began to proliferate as the technology began to be combined with conventional European chemical technology. The petrochemical industry swallowed up many of the existing mass-producing chemical industries and quickly assumed a key role among the other chemical industries.

It was at this time that Japan entered the petrochemicals arena. Since it already had mass-producing chemical industries in place, it was in a position to do more than simply adopt the new petrochemical technology being introduced; it took an active role in new technological innovations. Japan’s prior experience meant that by the late 1960s it was absorbing petrochemical technologies and successively developing its own. By the late 1970s, the intensive developments in petrochemical technology had eased, and petrochemistry began to spread across the developing nations. It was during this time that the negative aspects of petrochemistry began to emerge, such as environmental issues and chemical pollution issues. On top of this, the two oil crises in the 1970s escalated the cost of petrochemical products, resulting in a demand for low-emission technology and energy-conserving technology. By this time the Japanese petrochemical industry was no longer simply relying on technology imports and was developing its own technology. From the 1980s, the challenge was to develop olefins-based products with at least three carbon atoms, rather than ethylene products with two carbon atoms. The Japanese petrochemical industry was very active in this field. Petrochemistry became a substantial chemical industry with a wide range of products in its arsenal.

Meanwhile, significant changes started taking place on the petrochemical industrial world map with the emergence of the Middle Eastern petrochemical industry in the 1980s. This trend has accelerated since the 2000s with China entering the industry and huge increases in production. In the 2010s, the core of the petrochemical industry is taking a dramatic shift away from the West and towards Asia and the Middle East. Accordingly, Western companies have been successively dropping out of the industry since the 1990s. However, unlike their counterparts in the West, Japanese petrochemical companies took a different path. Japan is now not only planning for greater functionalization within the petrochemical industry, but also developing fields of functional chemistry outside of the conventional scope of petrochemistry, even incorporating polymer molding technology.

There have also been changes within the conventional scope of petrochemistry, such as significant growth in the demand for propylene in contrast to ethylene. In response to these changes in business environment, new trends have been observed in petrochemical technology since the 1990s. Petrochemistry may change significantly in the next decade or two.

■ Profile

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1967:	Graduated from Tokyo Metropolitan Ueno High School
1972:	Graduated from the Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo
1974:	Completed Master's degree at the Graduate School of Engineering, The University of Tokyo Joined the Ministry of International Trade and Industry (administrative post)
1987:	Joined Mitsui Toatsu Chemicals Co., Ltd.
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1 Introduction

Let us begin by defining petrochemistry and clarifying the scope of what is covered in this survey report.

1.1 Definition of petrochemistry

The petrochemical industry is often defined as “a chemical industry with petroleum as its raw material.” Certainly, petroleum is the main raw material used in the Japanese petrochemical industry. However, globally speaking, there are vast petrochemical industries in the United States and Middle East that use natural gas and associated petroleum gas as raw materials; it is therefore inaccurate to use a definition that only applies to the Japanese petrochemical industry. Furthermore, the above definition only qualifies the raw material used in an industry without determining to what extent the products produced in that industry can be products of the petrochemical industry.

Current chemical industries are structured as shown in Fig. 1.1. The petrochemical industry forms a core industry providing raw materials to low-molecular organic chemical end-product industries (pharmaceuticals, pesticides etc.) and high-molecular chemical end-product industries (plastic molding, chemical fibers, coatings, etc.).

As shown in Table 1.1, the chemical industries here are the chemical and allied product industries as defined by the Japan Standard Industrial Classifications, as well as plastic products, rubber products and chemical fibers (rayon, acetate, synthetic fibers). Although the chemical fiber industry was classified as a chemical industry up until the 2002 revision of the Japan Standard Industrial Classification, since then it has been classified as a textile industry. Out of consideration for continuity of statistics, production history and technical details, it has been included as a chemical industry for the purposes of this report.

In light of the current structure of the chemical industries, the petrochemical industry is defined in this report as “a chemical industry producing basic petrochemical products, industrial organic chemicals and polymers using petroleum or natural gas as the raw material.” The petrochemical industry spans a number of industries in the Japan Standard Industrial Classifications, namely: basic petrochemicals, aliphatic intermediates, cyclic intermediates, plastics, synthetic rubber and surface-active agents (surfactants). This definition is slightly broader than what is generally termed as petrochemistry, and includes industrial organic chemicals made from methane, engineering plastics and functional polymers, which have recently been developed into a number of different products.

However, since the petrochemical industry often refers to products with significantly high production and demand volumes, this report focuses on products within this broader definition that have high production and demand volumes.

1.2 Focus of the survey report

Present-day petrochemical products include vinyl chloride, polyvinyl chloride (PVC), synthetic surfactants, coating resins and adhesive resins. Some of these have been touched on in other technology systemization survey reports, such as the reports on vinyl chloride (March 2001, March 2002), soaps and synthetic detergents (March 2007), coating (March 2010) and adhesives (August 2012). The petrochemical industry has produced a great number of products and product groups with an equally impressive production scale, history and technology system, including methanol and its derivatives, olefins (including dienes), aromatics, alcohols, organic solvents, plasticizers, acetic acid, polyvinyl acetate and its derivatives, ethylene oxide and its derivatives, acrylonitrile and its derivatives, acrylic acid and its derivatives, methyl methacrylate and polymethyl methacrylate, polyethylene, polypropylene, styrene and styrenic polymers, phenol and its derivatives, phenol resin and amino resin, polyurethane and its raw materials, epoxy resin, unsaturated polyester resin, polyethylene terephthalate (PET) resin and its raw materials, polyamide resin (nylon resin) and its raw materials, engineering plastics, generic synthetic rubbers, special synthetic rubbers, thermoplastic elastomers, silicon resin and fluorine-based industrial organic chemicals and resins.

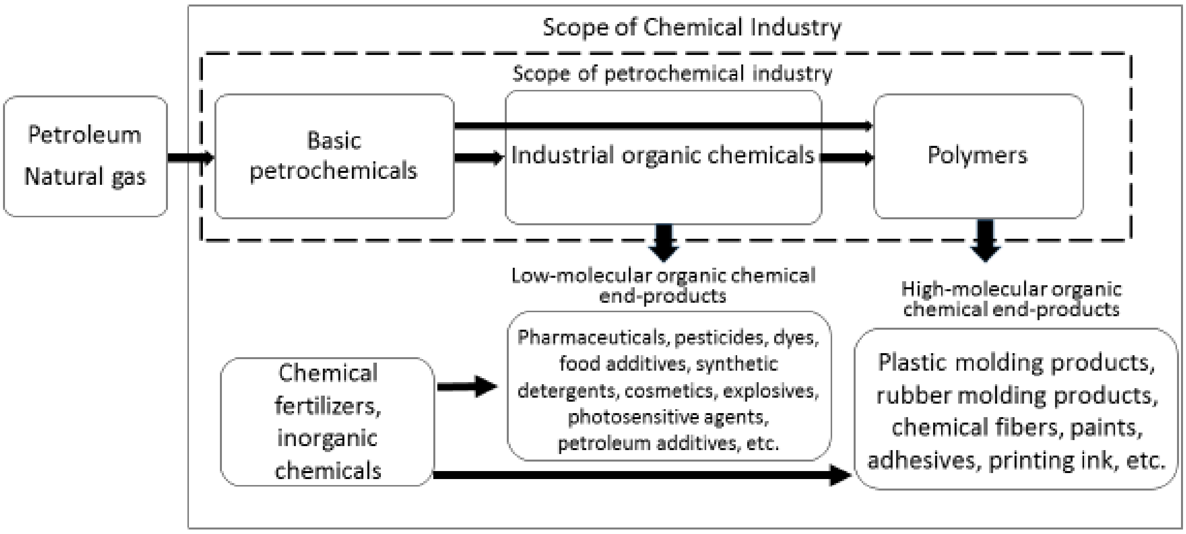
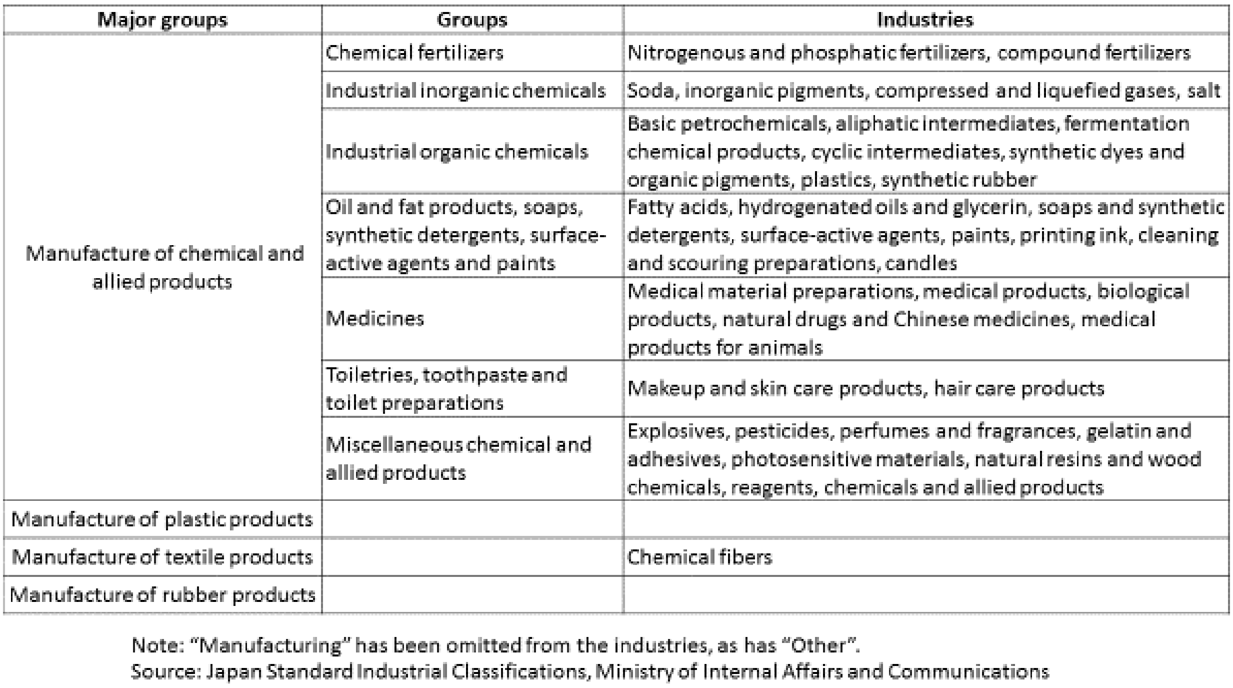


Fig. 1.1 Chemical industry and petrochemical industry.

Table 1.1 Definition of chemical industry



Major groups	Groups	Industries
Manufacture of chemical and allied products	Chemical fertilizers	Nitrogenous and phosphatic fertilizers, compound fertilizers
	Industrial inorganic chemicals	Soda, inorganic pigments, compressed and liquefied gases, salt
	Industrial organic chemicals	Basic petrochemicals, aliphatic intermediates, fermentation chemical products, cyclic intermediates, synthetic dyes and organic pigments, plastics, synthetic rubber
	Oil and fat products, soaps, synthetic detergents, surface-active agents and paints	Fatty acids, hydrogenated oils and glycerin, soaps and synthetic detergents, surface-active agents, paints, printing ink, cleaning and scouring preparations, candles
	Medicines	Medical material preparations, medical products, biological products, natural drugs and Chinese medicines, medical products for animals
	Toiletries, toothpaste and toilet preparations	Makeup and skin care products, hair care products
	Miscellaneous chemical and allied products	Explosives, pesticides, perfumes and fragrances, gelatin and adhesives, photosensitive materials, natural resins and wood chemicals, reagents, chemicals and allied products
Manufacture of plastic products		
Manufacture of textile products		Chemical fibers
Manufacture of rubber products		

Note: "Manufacturing" has been omitted from the industries, as has "Other".
Source: Japan Standard Industrial Classifications, Ministry of Internal Affairs and Communications

Supposing that olefins, vinyl chloride or the like were single trees, then petrochemistry would be an entire forest. Accordingly, surveying petrochemistry to the same depth as vinyl chloride or other technology systematization reports that have already been done would be impossible, not only in terms of the sheer number of hours and pages required, but also in terms of the capabilities of a single survey officer. It would also not be enough to simply focus on some of the as yet unreported areas of petrochemistry, such as olefins, phenol and its derivatives, or polyethylene, as then the overall picture of petrochemistry would be lost. Consequently, this survey report does not focus in on any particular area, instead providing a wide-angle view of the overall field of petrochemistry and discussing the wider trends of the entire forest. Readers should be advised that this report will not go into the same level of detail on the individual trees, so to speak, as has been done in other survey reports.

As a lead-up to the history of petrochemistry, this report does provide a relatively detailed outline of the industrial organic chemical and polymer industries that existed prior to the establishment of the petrochemical industry, using raw materials other than petroleum or natural gas, such as the coal chemical industry. These industries have now come under pressure from the petrochemistry industry and have diminished significantly. However, they are essential to any consideration of the history of petrochemical industry technology. They have been included in this report because there would be few other opportunities to include them in other technology systematization survey reports.

The petrochemical industry was founded in the United States of America in the 1920s and developed from there. Industries were established in Europe and Japan following a worldwide increase in Middle Eastern oil exports from the 1950s onwards. Since the 1970s, petrochemical industries have continued to expand all around the world. The raw materials, products and technologies of the petrochemical industry have been traded the world over since the 1950s. Accordingly, the development of the petrochemical industry in Japan must be viewed in the context of global trends; this survey report focuses the worldwide petrochemical industry as much as possible, rather than just Japan.

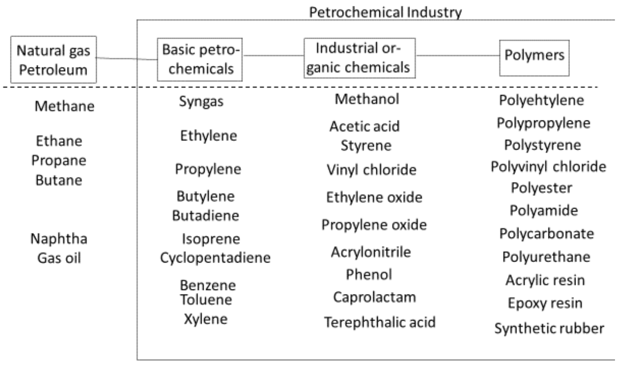
Please note that since this report is intended for the general public, the use of chemical structural formulas has been provided only for reference and the use of chemical reaction formulas has been avoided as much as possible.

2 Overview of petrochemistry

This chapter provides an overview of petrochemistry. What are petrochemical products? What are they used for? How does the petrochemical industry relate to society and to other industries? What are the distinguishing characteristics of the production technology? What other technologies have been based on petrochemical technology and what related technologies undergird petrochemistry? These are the points that shall be addressed.

2.1 Uses of petrochemical products

Petrochemical products can be divided into three major categories, as shown in Fig. 2.1. These are basic petrochemicals, industrial organic chemicals and polymers. Figure 2.1 also shows some of the main products in each of these categories. However, there are actually far more products than those given here.



Petrochemical Industry

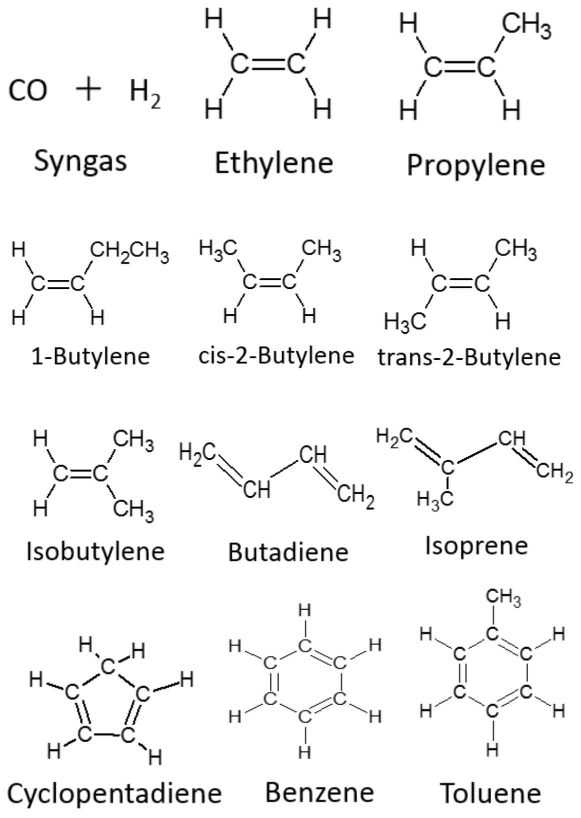
Natural gas Petroleum	Basic petro- chemicals	Industrial or- ganic chemicals	Polymers
Methane Ethane Propane Butane Naphtha Gas oil	Syngas Ethylene Propylene Butylene Butadiene Isoprene Cyclopentadiene Benzene Toluene Xylene	Methanol Acetic acid Styrene Vinyl chloride Ethylene oxide Propylene oxide Acrylonitrile Phenol Caprolactam Terephthalic acid	Polyehtylene Polypropylene Polystyrene Polyvinyl chloride Polyester Polyamide Polycarbonate Polyurethane Acrylic resin Epoxy resin Synthetic rubber

Fig. 2.1 Current raw materials and principal products of the petrochemical industry.

2.1.1 Uses of basic petrochemicals

The main use for basic petrochemicals with a one carbon atom (C1) (syngas, carbon monoxide, phosgene, hydrogen cyanide, chloromethane) is as the raw materials for industrial organic chemicals. A small amount is used as organic solvents and also as a raw material for industrial inorganic chemicals.

Basic petrochemicals with two or more carbon atoms can be divided into two broad categories: olefins [Footnote 1] and aromatic hydrocarbons. Aromatic hydrocarbons are hydrocarbons with a relatively stable carbon ring (aromatic ring) [Footnote 2]. Typical products include benzene (C6), toluene (C7) and xylene (C8). Olefins are hydrocarbons with double bonds and no aromatic ring. Typical products include ethylene (C2, one double bond), propylene (C3, one double bond), butylene (C4, one double bond), butadiene (C4, two double bonds), isoprene (C5, two double bonds) and cyclopentadiene (C5, cyclic structure, two double bonds) [Footnote 3]. The molecular structures of some typical basic petrochemical products are shown in Fig. 2.2 for reference.



[Footnote 1] A compound comprising only carbon and hydrogen is called a hydrocarbon. As the number of carbon bonds and bonding methods can vary greatly, there are an almost unlimited number of different hydrocarbons. Hydrocarbons with one or more double bonds are called olefins. Hydrocarbons with only one double bond are also called alkenes. Double bonds are more reactive than single bonds

[Footnote 2] Typical examples are benzene rings, with six carbons joined in a ring, and naphthalene rings. Aromatic rings themselves are very stable and do not break easily. Atoms or functional groups attached to the edge of an aromatic ring are more susceptible than to substitution reactions or oxidation reactions than the carbon-carbon bonds forming the aromatic ring.

[Footnote 3] Other than cyclopentadiene, the typical olefins-based products mentioned have a linear carbon structure (and are capable of branching). Cyclopentadiene has five carbon atoms in a cyclic structure. See Fig. 2.2 for the chemical structural formula.

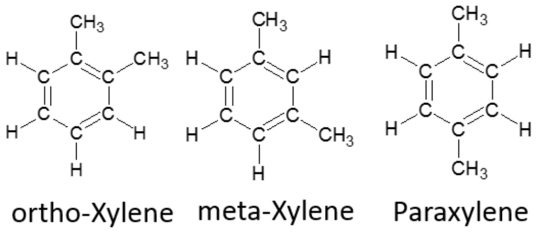


Fig. 2.2 Molecular structures of typical basic petrochemicals.

In principle, there are many other hydrocarbons besides these with eight or less carbon atoms. This also includes some substances produced by steam cracking of naphtha, as shall be mentioned later. However, these are seldom used as basic petrochemical products as they do not have any widespread applications and the separation and purification process is a difficult one.

Thus, even including isomers [Footnote 4], there are no more than around a dozen basic petrochemical products at most that are being put to use in large quantities. The only use for basic petrochemical products is to provide the raw materials for industrial organic chemicals and polymers. Olefins are often consumed as raw materials (monomers) for polymers without being made into industrial organic chemicals. Of all of the petrochemical products produced worldwide, around 60% of ethylene is estimated to be consumed as polyethylene, 60% of propylene goes into polypropylene (PP) and synthetic ethylene-propylene rubber (EPR), at least 90% of butadiene goes into styrene-butadiene rubber (SBR), butadiene rubber (BR), acrylonitrile-butadiene rubber (NBR) and other synthetic rubbers, as well as acrylonitrile-butadiene-styrene resin (ABS resin) [Footnote 5]. The remaining 40% of ethylene and propylene goes into a very wide variety of industrial organic chemicals.

Meanwhile, aromatic hydrocarbons are almost never used in polymers directly; they provide the raw material for industrial organic chemicals. Other than industrial organic chemicals, another major application for these is in solvents. Benzene, toluene and mixed xylene (xylene isomer mixture) are used in solvents.

2.1.2 Uses of industrial organic chemicals

Industrial organic chemicals are made by reacting basic petrochemical products together, or by reacting them with inorganic chemicals, such as air, oxygen, hydrogen, water, ammonia, chlorine, sulfuric acid or nitric acid. Unlike basic petrochemical products, there is an extremely diverse range of industrial organic chemicals with various chemical and physical properties. The products shown in Table 2.1 are just a very few examples of industrial organic chemical products with particularly high production volumes.

To a certain extent, industrial organic chemicals can be broadly categorized by functional group [Footnote 6]. Table 2.1 shows examples of types and products of typical industrial organic chemicals categorized by functional group. Fig. 2.3 also shows examples of typical functional groups along with chemical structural formulas of typical products. Since the chemical properties of industrial organic chemicals largely depend on the functional group, these categorizations can provide a general idea of their application and method of production. For example, many alcohols are used directly as solvents and have esters or ethers as their feedstock. As epoxides have very reactive three-membered rings containing oxygen, they are used to produce other industrial organic chemicals or in polymerization reactions. In many cases, a single industrial organic chemical has multiple applications, being used as an organic solvent as well as an organic intermediate.

[Footnote 4] Some substances have different chemical and physical properties despite having the same molecular formula, due to having different chemical structures. The substances are called isomers. For example, there are four isomers of butylene with four carbon atoms and three isomers of xylene with eight carbon atoms, as shown in Fig. 2.2. Including the similarly-structured ehtylbenzene, there are four such isomers.

[Footnote 5] Since the Japanese petrochemical industry supplies a diverse range of products, around 40% of ethylene and propylene is consumed only as polyethylene and PP.

[Footnote 6] An atom or group of atoms that determines the properties of an organic compound is called a functional group. For example, the alkyl group, which is composed of only carbon and hydrogen, carries the properties of being hydrophobic and having relatively low reactivity. The hydroxyl group, composed of oxygen and hydrogen, carries the property of being hydrophilic. The chloro group carries the property of being flame retardant.

Table 2.1 Typical industrial organic chemical types and products

Type	Example products
Hydrocarbons	Cyclohexane, ethylbenzene, cumene, benzene, styrene, α-olefins, propylene oligomer, alkylates
Alcohols	Methanol, ethanol, isopropyl alcohol, tert-butyl alcohol, sec-butyl alcohol, 2-ethylhexyl alcohol, higher alcohols, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, glycerin, propylene glycol, polypropylene glycol, cyclohexanol, pentaerythritol
Aldehydes	Formaldehyde, acetaldehyde, acrolein, n- butyraldehyde, isobutyraldehyde
Ketones	Acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), cyclohexanone, anthraquinone
Epoxides (3-membered ring ethers)	Ethylene oxide, propylene oxide, epichlorohydrin
Ethers	Dimethyl ether, diethyl ether, glycol ethers, propylene glycol ether, MTBE, polyoxyethylene alkyl ethers, THF
Carboxylic acids	Acetic acid, acrylic acid, fumaric acid, adipic acid, terephthalic acid, EDTA
Esters	Acetic acid esters, vinyl acetate, acrylic acid esters, methyl methacrylate, ethylene carbonate, phthalic acid esters, phosphoric acid esters, higher alcohol sulfuric acid ester salt
Acid anhydrides	Maleic anhydride, phthalic anhydride, acetic anhydride
Amides	DMF, DMAc, acrylamide, caprolactam, N-methylpyrrolidone
Amines	Monoethanolamine, ethylenediamine, hexamethylenediamine, aniline, p-phenylenediamine, meta-phenylenediamine, alkyl amines, aliphatic quaternary ammonium compounds
Nitriles	Acrylonitrile, adiponitrile, acetonitrile
Isocyanates	TDI, MDI, HMDI, isophorone diisocyanate
Phenols	Phenol, bisphenol A, alkyl phenols, hydroquinone, resorcinol
Chlorinated organic compounds	Chloromethanes, ethylene dichloride, vinyl chloride, vinylidene chloride, trichlorethylene, tetrachlorethylene, allyl chloride, epichlorohydrin, chlorobenzene, dichlorobenzene, chloroprene
Sulfur-containing organic compounds	Alkylbenzene sulfonic acids, DMSO, sulfolane

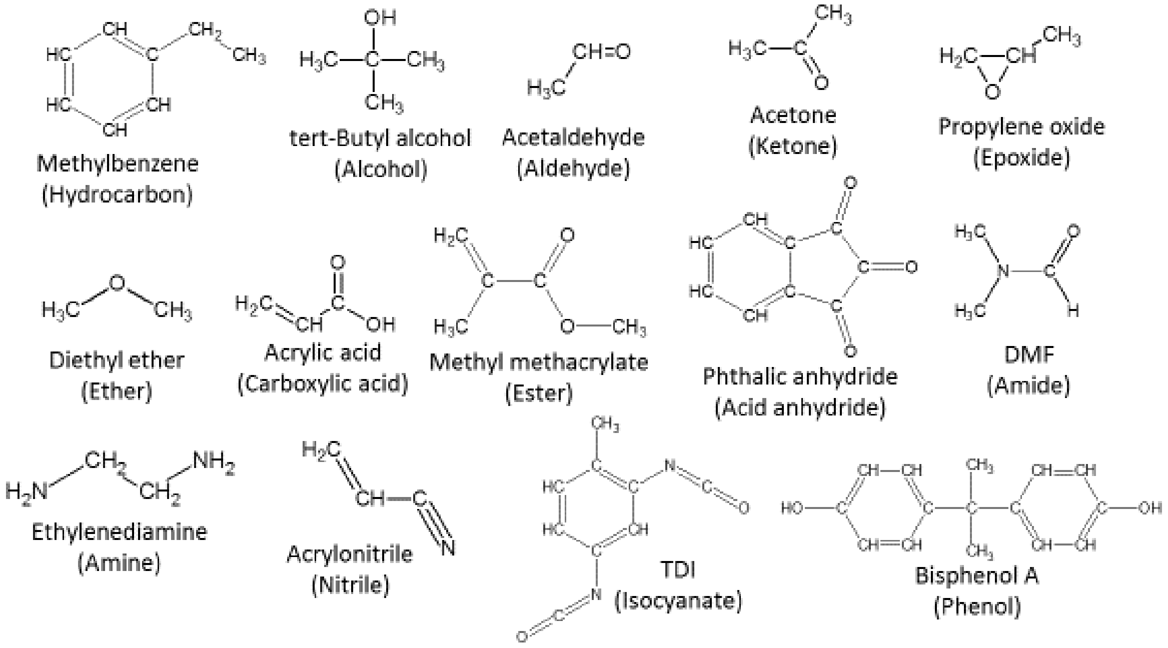


Fig. 2.3 Examples of typical functional groups and molecular structures of industrial organic chemicals.

As shown in Table 2.2, the main uses for industrial organic chemicals are monomers (feedstocks for polymers), organic solvents, refrigerants, heat transfer medium, plasticizers, surfactants, organic intermediates and other uses.

(1) Monomers (feedstocks for polymers)

Quantitatively, the most common application by far for industrial organic chemicals is monomers. There are four types of monomers, as shown in Table 2.2. Carbon-carbon double-bonded monomers form polymers through a reaction whereby the double bond becomes a single bond, and the monomers join together. Cyclic monomers form polymers through the opening of the ring. Monomers with multiple functional groups within one molecule form polymers through a reaction between functional groups that creates new bonds. For example, ethylene glycol (EG) is a type of alcohol and has two hydroxyl groups. High-purity terephthalic acid (PTA) is a carboxylic acid and has two carboxyl groups. The hydroxyl groups and carboxyl groups react, releasing water and forming an ester linkage. When EG and PTA form an ester linkage on a molecule, a hydroxyl group and a carboxyl group form at the ends of the molecule, and the EG and PTA can react further. The same thing happens even when larger molecules produced react together. Thus, the molecule grows and forms a polymer. Monomers with multiple reactive sites act the same way as monomers with multiple functional groups, with reactive sites reacting to form new bonds and creating a polymer. For example, phenol has three reactive sites, and formaldehyde has two reactive sites.

Table 2.2 Typical industrial organic chemical applications and example products

Application	Type	Example Products
Monomers	Double-bonded	Styrene, vinyl chloride, vinyl acetate, acrylic acid, acrylic acid esters, methyl methacrylate, vinylidene chloride, acrylonitrile
	Cyclic-bonded	Ethylene oxide, propylene oxide, epichlorohydrin, caprolactam
	Multiple functional groups	Ethylene glycol, 1,4-butanediol, glycerin, polypropylene glycol, pentaerythritol, hexamethylenediamine, adipic acid, terephthalic acid, maleic anhydride, phthalic anhydride, TDI, MDI, HMDI, isophorone diisocyanate, bisphenol A, dichlorobenzene
	Multiple reactive sites	Phenol, formaldehyde
Organic solvents, refrigerants, heat media, plasticizers		Cyclohexane, methanol, ethanol, acetone, MEK, diethyl ether, glycol ethers, DMF, DMAc, N-methylpyrrolidone, DMSO, THF, trichlorethylene, tetrachlorethylene, chlorobenzene, phthalic acid esters, phosphoric acid esters
Surfactants		Alkylbenzenesulfonic acids, polyoxyethylene alkyl ethers, alkyl amines, aliphatic quaternary ammonium compounds
Organic Intermediates		Acetaldehyde, methylene dichloride, alkyl benzenes
Other (fuel, petroleum additives, etc.)		Alkylates, MTBE, dimethyl ether

(2) Organic solvents, refrigerants, heat transfer mediums, plasticizers

Not only are organic solvents used in the chemical industry (reaction solvents, synthetic fiber spinning solvents, extraction solvents, etc.), they are also used in large quantities in the machinery industry (degreasing agents for machine parts processing, and cleaners for semiconductor manufacturing, refrigerants and heat transfer mediums, etc.) and the laundry industry (dry cleaning) as well. They are also used as components in chemical products, such as coatings, adhesives, printing inks, aromas, cosmetics and pesticides. Furthermore, they have also recently started being used as a component (electrolyte solution) in lithium-ion secondary batteries. Plasticizers are liquid organic chemical products with high boiling points; these are used to soften polymers and to improve moldability.

(3) Surfactants

A large amount of surfactants are used in synthetic detergents. They also have a wide range of other applications, such as fabric softeners, concrete water-reducing agents, disinfectants, foaming and antifoaming agents and solubilizers and emulsifiers for cosmetics and pesticides.

(4) Organic intermediates

Organic intermediates are solely used as feedstocks for other industrial organic chemicals, such as ethylbenzene, feedstock for styrenes, cyclohexane, feedstock for caprolactam and adipic acid and ethylene dichloride, feedstock for vinyl chloride and chlorinated solvents. These form a substantially high volume of products. Some organic intermediates are also used as feedstocks in chemical industries outside of the petrochemical industry, pharmaceuticals, pesticides and dyes. There are numerous different types of these organic intermediates, although the individual types are not very substantial in volume.

(5) Other uses

Other applications that use high volumes of industrial organic chemicals are gasoline feedstocks and petroleum additives, such as alkylates [Footnote 7] and methyl tertiary butyl ether (MTBE). Alkylates are produced by oil refineries and are often self-consumed.

2.1.3 Uses of polymers

Substances with a molecular weight of around 1,000 or higher are called polymers. Since polymers are formed by monomers, substances with a low molecular weight, going through a very large number of reactions, their molecular structure is made up of a very long series of repeated units. The reaction that produces polymers is called polymerization.

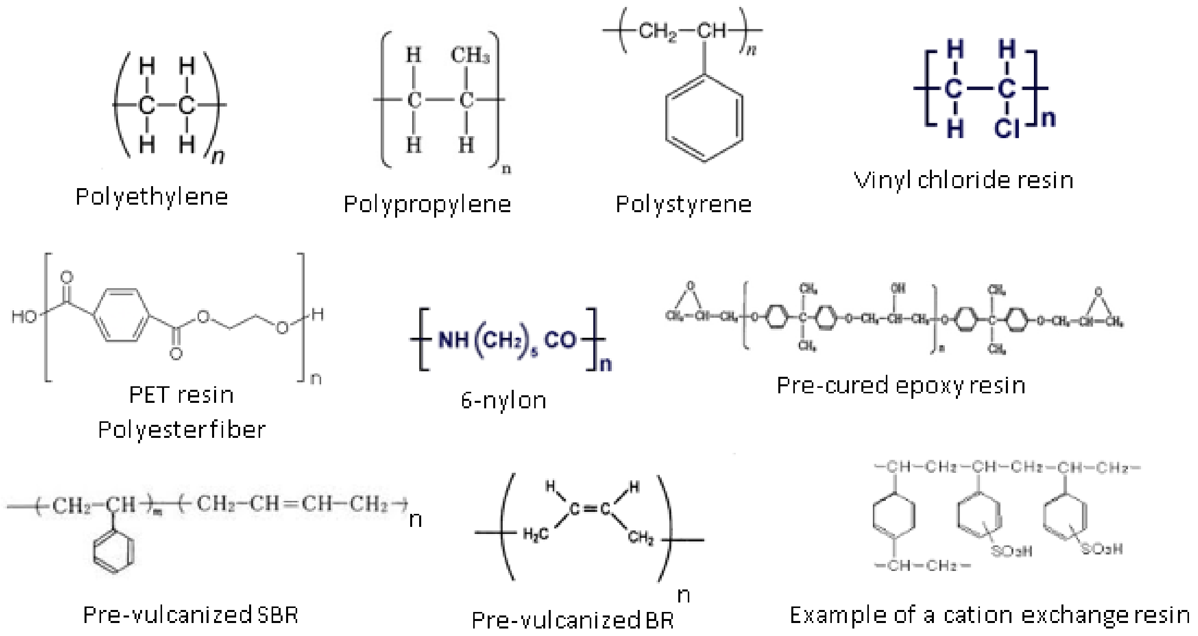
There are a very high number of different types of polymers, although they are not as numerous as industrial organic chemicals. Polymers can be classified in various ways, such as by molecular structure, by polymerization method or by application. For reference, Fig. 2.4 shows the molecular structures of some typical polymers. Table 2.3 shows a classification of polymers by application. Polymer applications can be categorized into molding products, coatings, adhesives and binders and high performance products. In this report we shall only cover molding products, since these account for the highest volume by far.

Molding products can be divided into three broad categories: plastic molding products, synthetic fibers and rubber molding products.

(1) Plastic molding products

While the term plastic can refer to any material that can be molded into a desired shape (any material with plasticity), nowadays it is generally only used to describe polymers. Plastics can be grouped into thermoplastics and thermoset plastics. Thermoplastics are polymers that soften or fluidize when heated. These are molded while hot and form the finished product once cooled. If the finished product is heated again, it softens or melts. Conversely, thermoset plastic finished products no longer soften or melt, even when heated again. Thermoset plastics are molded at the raw material stage while the molecular weight is low and the material has some fluidity, or at a semi-polymer stage when the molecular weight has increased to a certain extent. After molding, the product is then heated to complete the reaction further, resulting in the finished product. The reaction that takes place through heating after molding links the polymers together in three dimensions (crosslinking).

[Footnote 7] Gasoline base materials that are multi-branch chain saturated hydrocarbon mixtures made by reacting isobutene with propylene, butylene or other olefins.



Polyethylene

Polypropylene

Polystyrene

Vinyl chloride resin

PET resin
Polyesterfiber

6-nylon

Pre-cured epoxy resin

Pre-vulcanized SBR

Pre-vulcanized BR

Example of a cation exchange resin

Fig. 2.4 Typical polymer chemical structures.

Table 2.3 Polymer applications and example products

Applications			Example Products
Molding products	Plastic molding	Thermoplastics	Polyethylene, polypropylene, styrene resins, vinyl chloride resins, PET resins, methacrylate resins, engineering plastics
		Thermoset plastics	Polyurethanes, epoxy resins, phenolic resins, unsaturated polyester resins, acrylic resins, silicon resins, fluororesins
	Synthetic fiber		Nylon, polyester, acryl, polyethylene, polypropylene, polyurethane, aramid
	Rubber molding	Vulcanized	SBR, BR, EPDM, NBR, IR, butyl rubber, special rubbers
		Thermoplastic	Thermoplastic elastomers (styrene, polyolefin, polyurethane)
Paints, adhesives, binders			Phenolic resins, polyurethanes, epoxy resins, polyacrylic acid ester, polyvinyl acetate, EVA resins, alkyd resins, synthetic rubbers, silicone resins, fluorine resins
High performance products			Ion exchange resins, chelate resins (styrene-sulfonate divinylbenzene copolymer, quaternary ammonium salts, iminodiacetic acid salts, sodium polyacrylate) Flocculants (polyacrylamides) Dispersing agents (sodium polyacrylate, polyvinyl alcohol) Thickeners (polyacrylamide, xanthan gum) Photosensitive polymers (photoresist, printing plate making, dental materials, inks, coatings)

Since the molding stage generally allows thermoplastics to have a far greater productivity than thermoset plastics, thermoplastics have far higher production volumes. These categorizations are not absolute, as the same polymer can be made into a thermoplastic or a thermoset plastic, depending on the molecular design of the polymer structure and on how the polymerization and molding are achieved. For example, polyethylene is very commonly used as a thermoplastic; however, in some cases it is used as a thermoset plastic, being crosslinked to form a three-dimensional structure after molding, such as for high-voltage cables and for water supply and hot water piping. Polyurethane is also often used as a thermoset plastic, and the polyurethane foam used in cushions is a thermoset plastic product. However, thermoplastics with one-dimensional molecular structures are used for synthetic fibers.

(2) Synthetic fibers

Synthetic fibers are made from polymers with one-dimensional structures that are easily crystallized. After forming the fiber shape, they are stretched to increase the degree of crystallinity, which significantly increases the tensile strength of the fiber. Synthetic fibers can be treated as a type of thermoplastic molding product.

(3) Synthetic rubber molding products

Synthetic rubbers are materials with so-called rubber elasticity. Rubber molecules have a far looser molecular structure at room temperature than plastic molecules. Therefore, when stretched, their tensile strength decreases considerably and they expand significantly. Since the rubber molecules are crosslinked to each other and the molecular chain does not shift, when the stretching force is released, the rubber immediately returns to its former shape. Thus, rubbers differ significantly from plastics in terms of their physical properties. Synthetic rubbers are molded in a softened state. At that stage, sulfur and crosslinking agents are kneaded in. After molding, a vulcanization reaction occurs upon heating. This is the same as the crosslinking reaction in thermoset plastics. The sulfur and crosslinking agents link the rubber molecules together and the elastic properties emerge.

By contrast, like thermoplastics, thermoplastic elastomers melt when heated and can be molded. Once cooled, this forms a molding product with elastic properties. There is also no need to add sulfur and crosslinking agents or to induce a vulcanization reaction by heating. These synthetic rubbers are high in productivity due to the molding process.

2.2 Interaction between the petrochemical industry and other industries and society

The petrochemical industry has had various interactions with other chemical industries, other industries and also wider society. The following is a brief outline of the history of the petrochemical industry in Japan as an example.

2.2.1 The polymer revolution

The petrochemical industry became industrialized in Japan in the late 1950s, mainly through introduced technology from the West. By the end of 1960s, the industry was supplying large volumes of new products, such as polyethylene, polystyrene, polypropylene (PP), polyester fiber, acrylic fiber and SBR.

On top of this, changes in raw materials and manufacturing methods in the 1960s saw the petrochemical industry take up and significantly develop new product categories that had been previously supplied by other chemical industries, such as nylon fiber, polyvinyl chloride, vinylon fiber, acetates and plasticizers. The petrochemical industry expanded by thus supplying large quantities of polymers to society, having a significant impact both on society and on other industries. Polymers had steadily spread across the United States throughout the 1930s–1950s and took Japan by storm in the late 1950s with the introduction of the petrochemical industry, sparking a polymer revolution in Japanese society. In addition, petrochemical industry production volumes skyrocketed from the late 1950s to the 1960s; this required large-scale capital investments to fund it, and played a hand in spurring Japan’s rapid economic growth. From the 1970s onwards, this pattern repeated again and again with the establishment of petrochemical industries in Korea, Taiwan, the ASEAN nations and even China.

Polymers advanced into new territories that had previously been the domains of wood, paper, natural fiber, natural rubber, glass, ceramics and metals. Polymers had the advantages of being lightweight, moldable, water resistant and corrosion resistant. They were initially used in a number of applications, including fibers, packaging/containers, daily necessaries, agricultural film, tires and wire coating. Later, they also came to be used in applications requiring higher strength and durability, such as construction, civil engineering, machine parts, fishing vessels, large-scale tanks and optical fibers. Currently, they are even being used in aircraft fuselages. Thus, polymers have made a significant contribution to energy conservation, product longevity and cost reduction in many industries, including manufacturing, distribution, transport and communications and the information industry.

2.2.2 Structural changes in the chemical industry

While the Japanese petrochemical industry was achieving considerable growth within the first two decades of its establishment, the wider Japanese petrochemical industry was also undergoing significant structural changes, in which the petrochemical industry came to take a leading role. The coal chemical industry (the acetylene chemical industry and coal tar chemical industry) and the fermentation chemical industry (ethanol fermentation industry and acetone-butanol fermentation industry), suddenly went into decline at the end of the 1960s, despite both having predated the establishment of the petrochemical industry. The celluloid industry, which had been one of Japan’s leading chemical industries since the 1910s, using cellulose (natural polymer) from wood/pulp as a raw material, and the rayon/acetate industry went into decline in the 1960s under pressure from the new plastics and synthetic fibers that were being produced by the petrochemical industry.

By contrast, polymer molding industries, such as plastic molding, rubber molding and synthetic fibers, were expanding dramatically due to the high-volume supply of low-cost plastics, synthetic rubbers and synthetic fibers.

Even the soap industry, which used natural fat as a raw material, went into decline due to pressure from the synthetic detergent industry, which used synthetic surfactants supplied by the petrochemical industry as its main raw material. The paint industry, which had similarly used natural fats and oils as raw materials, also transitioned to synthetic polymers as raw materials. Synthetic dyes, synthetic pharmaceuticals, cosmetics, pesticides and other chemical industries that had used coal chemical products and natural products as raw materials likewise transitioned to using petrochemical products as raw materials.

2.2.3 Location changes in the chemical industry

The Japanese petrochemical industry was established using naphtha (a petroleum distillate with a boiling point between 30–200°C) as a feedstock; the naphtha was supplied by oil refineries refining and separating crude oil imported mainly from the Middle East. The steam cracking of naphtha produced a number of liquid and gas basic petrochemical co-products. Costs were reduced by piping these products to adjacent industrial organic chemical plants and polymer plants. At that time, it was important that all of the basic petrochemical co-products were used up. Accordingly, the Japanese petrochemical industry took the form of a coastal industrial complex or *kombinat*, incorporating multiple chemical plants on an expansive site, right from the outset.

Until then, the chemical industries in Japan had used coal, electricity (mainly hydroelectric) and agricultural produce as raw materials, and had developed separately in different inland areas where those raw materials could be obtained [Footnote 8]. These existing chemical industries were forced to move to coastal industrial complexes by the petrochemical industry at the point where the raw materials were converted into petrochemistry. Many high-producing inorganic chemical industries, such as ammonia, industrial gas (oxygen, nitrogen, etc.) and salt electrolysis (chlorine, sodium hydroxide), have a far longer history than the petrochemical industry. Since the petrochemical industry requires large amounts of ammonia, oxygen, nitrogen and chlorine, as well as the carbon source, many of these inorganic chemical industries also started relocating to coastal industrial complexes as the petrochemical industry began to grow in scale. Thus, the

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[Footnote 8] Some of the coal chemical industries and electrochemical industries also had factories in the form of industrial complexes to maintain their product chains.

petrochemical industry effected significant structural changes in the geographic mapping of Japan’s chemical industries, with industries centering on the petrochemical industrial complexes.

2.2.4 Pollution/environmental issues and responses

Meanwhile, as the petrochemical industry developed, expanded in scale and centralized, its negative impacts on society also began to emerge. These included industrial pollution issues, plastic waste issues, chemical pollution issues and global environmental issues. To manage these, Japan carried out intensive emergency-response anti-pollution measures within a short period in the 1970s. From the 1980s onwards, these were followed by technology developments to revolutionize the chemical reaction processes from the ground up and to develop substitute products. The problem of plastic waste has been difficult to resolve, but the cooperation of society (such segregated collection and waste power generation) and other industries (such as the cement and steel industries) has now finally led to some progress towards a resolution, mainly through thermal recycling and material recycling.

2.2.5 Contribution to energy conservation

The two oil crises of the 1970s significantly impacted the petrochemical industry, not only in Japan, but all over the world. This prompted the development of energy-conserving technologies within the petrochemical industry, such as gas phase linear low-density polyethylene (L-LDPE) production technology. Meanwhile, lightweight plastics were becoming widespread throughout the automotive and aircraft industries, thereby improving the energy efficiency of cars and airplanes. Plastics with superior thermal insulation performance were being promoted as insulation in refrigerators, buildings and residential facilities. Thus, the petrochemical industry made a major contribution to social and industrial energy conservation through its products.

2.3 Undergirding technologies for the petrochemical industry

Petrochemistry is said to have had the United States as a mother, and Germany as a father. This refers to the fact that petroleum refining technology was developed in the United States, and that industrial organic/industrial inorganic chemicals and large-scale synthesis technology for synthetic oil were developed in Germany, as well as referring to polymer synthesis technology, such as the industrialization of synthetic rubber, which also started in Germany. These technologies laid the foundation for the establishment of the petrochemical industry. The technologies that formed the basis for the establishment and development of petrochemistry can be broadly grouped into four main areas, as shown in Fig. 2.5. Essentially, petrochemistry is an organic chemical industry; accordingly, organic chemistry technology plays the most significant role in undergirding it. However, this goes without saying and can be overlooked here.

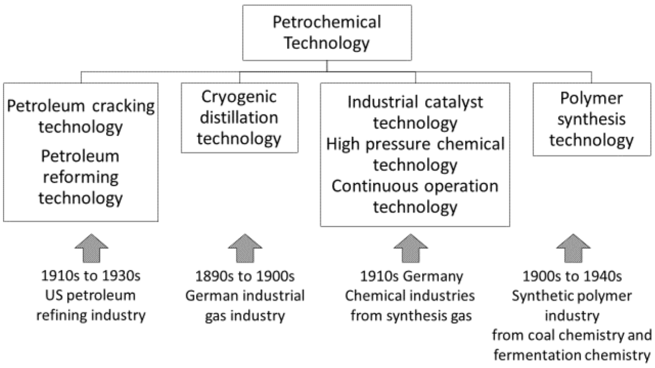

Fig. 2.5 Undergirding technologies for the petrochemical industry.

2.3.1 Petroleum cracking technology and petroleum reforming technology

Petroleum cracking technology and petroleum reforming technology were developed in the United States as a means of obtaining as much good-quality gasoline as possible from crude oil. These are related to steam cracking technology and aromatic hydrocarbon production technology, and form the core technologies for producing basic petrochemical products.

2.3.2 Cryogenic distillation technology

German company Linde AG completed an industrial air liquefaction equipment in 1895. This was followed by initiatives to develop cryogenic distillation technology, with devices developed for pure oxygen in 1902, pure nitrogen in 1903 and a two-column device for both pure oxygen and pure nitrogen in 1910. At the time, pure oxygen was used for welding and cutting; in the middle part of the 20th century, it started being used in large quantities in converter furnaces. Pure nitrogen was used to produce nitrolime, and also in ammonia synthesis. Cryogenic distillation technology was later used to separate hydrogen from syngas and water gas; the hydrogen was used in the hydrogenation of fats and oils and as a raw material in ammonia synthesis.

This kind of cryogenic distillation technology was essential in petrochemistry. In particular, accurate separation of different gases was very important in the steam cracking of naphtha. Distillative separation of ethane from natural gas, as well as precise distillation separation of ethane and ethylene, and propane and propylene, is the most prominent example of how cryogenic distillation technology underpins petrochemistry.

2.3.3 Industrial catalyst technology, high-pressure technology and continuous operation technology

Industrial catalyst technology and high-pressure technology, starting with ammonia synthesis in the 1910s, have come increasingly into play in petrochemical technology. Across the history of petrochemistry, nearly all new products and processes have come about due to the development of new industrial catalysts. At the same time, high-pressure technology laid a significant milestone in petrochemistry with high-pressure low-density polyethylene production technology in the 1930s. Reactions under high pressure have been established as one of the fundamental petrochemical technologies, although not to such a high pressure as this. Petrochemical equipment often used in high-pressure chemistry is extremely compact and highly productive.

Meanwhile, continuous operation technology for successively reacting and also separating and purifying large volumes of gases and liquids can be traced back to 1867, with the Solvay process (ammonia-soda process). However, it was technologies developed for ammonia synthesis, methanol synthesis and synthetic oil that laid the immediate foundation for the continuous processes widely used in petrochemistry.

2.3.4 Polymer synthesis technology

For the first couple of decades of its establishment in the United States, petrochemistry was mainly used for products such as solvents, petroleum additives and antifreeze. However, a push for the production of synthetic rubber in the United States in the 1940s formed the first links of the polymer industry with petrochemistry, and significant development began on the petrochemical industry in the United States. Even today, as mentioned previously, polymers make up for an overwhelmingly high proportion of basic petrochemical product consumption and industrial organic chemical consumption. By linking with polymers, petrochemistry has transformed into a materials-supply industry, and a large-scale industry at that. Most of the polymer synthesis technology already achieved by the 1940s involved monomers produced by the coal chemical industry or the fermentation chemical industry. These technologies were incorporated into petrochemistry and became fundamental technologies of the petrochemical industry. In the 1950s, Europe also entered the petrochemical era, with large quantities of olefin being supplied. Ziegler-Natta catalysts were discovered in Europe at that same time, and this new polymer synthesis technology became the first polymer technology in petrochemistry. This technology later resulted in a great leap forward in petrochemistry.

2.4 Related technologies that support petrochemistry

As mentioned several times previously, petrochemical technology was introduced to Japan in the late 1950s. A lot of related supporting technology was also introduced to Japan at the same time. There were four main technologies, as shown in Fig. 2.6. This was also a time of breakthrough in these technologies that were essential to petrochemistry. In that sense, petrochemistry became industrialized in Japan with very good timing.

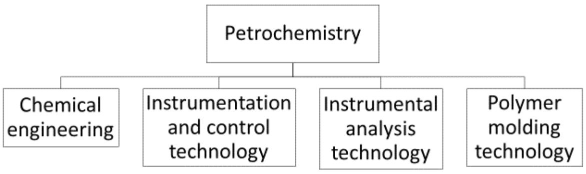

Fig. 2.6 Related technologies that support petrochemistry.

However, not all chemical companies adopted these related technologies. If we look at the history of various chemical companies, we see that in the early 1950s many of them investigated the American petrochemical industry and petrochemical technology and considered whether or not to enter the market. At that time, there was often a strong sense of resistance to petrochemical technology and also related technologies among chemical companies experienced in batch reactions, such as synthetic dyes. This was due to differences between science-type chemical corporate culture and engineering-type chemical corporate culture. In many cases, these differences in corporate culture resulted in companies failing or lagging behind in introducing petrochemistry.

2.4.1 Chemical engineering

Chemical engineering was developed in the 1910s by the American oil refining industry. It developed as an academic discipline focused on physical operations that are utilized across the oil refining and chemical industries, such as flow (fluid transport, filtration), thermal conductivity and mass transfer (gas absorption, distillation, extraction, drying, adsorption). Arthur D Little from the United States advocated the idea of unit operation; chemical engineering was established once it was incorporated into the education curriculum. By the end of the 1920s, unit operation had a greater amount of substance, such as the completion of distillation theory, and it began to be utilized by the American oil refining industry and also the petrochemical industry as well. Further developments were also taking place in process engineering, which examines the oil refining process and chemical processes overall, and reaction engineering, which focuses on the core reaction part of the process. Chemical engineering became an essential technology, not only in terms of designing, procurement, managing construction and operation of individual petrochemical facilities, but also for planning and designing complete factories and overall industrial complexes.

German-style industrial chemistry and applied chemistry had also been taught in Japan since the start. However, this was fundamentally different from the systems-engineering nature of chemical engineering. Although organizations such as Kanazawa Higher School of Technology (now Kanazawa University), Kyoto University and Tokyo Institute of Technology had established chemical machinery and chemical engineering departments by around 1940, chemical engineering was not yet widely known about in the Japanese chemical industry. In the 1950s, petrochemical technology and chemical engineering were both adopted by the Japanese chemical industry, and the idea of chemical engineering was welcomed with new wonder. Today, chemical engineering has taken hold in many fields of the chemical industry besides petrochemistry and is becoming a key technology right across the chemical industry.

2.4.2 Instrumentation and control technology

Instrumentation and control is technology to operate a plant using three factors: measurements by measuring instrumentation, automated feedback control and automatic valves. When petrochemistry was introduced to Japan, instrumentation and control technology was transitioning from pneumatic control to electronic control, and the technology was becoming more compact and more long-range. Accordingly, Japan’s new petrochemical plants built central control rooms for monitoring and control. This method of operation, called process automation, had not been available to the existing chemical industries in Japan. The petrochemical industry and the oil refining industry were the first to implement automated production processes.

2.4.3 Instrumental analysis

The late 1950s, when petrochemistry was introduced to Japan, was the time in which technologies to support petrochemistry were just coming into full swing; instrumental analysis technology was no exception. Gas chromatography and infrared spectroscopy are often used in petrochemistry. In gas chromatography, analysis is made by separating out gaseous components and easily-vaporized liquid components; in infrared spectroscopy, organic compounds are analyzed by functional group. The world’s first gas chromatograph was introduced in 1955; by 1957, Japan had developed its own mass-produced gas chromatograph equipment. By 1958, the process gas chromatograph was being developed. By 1957, a high-resolution infrared spectrophotometer had also been developed.

While these analysis devices were initially expensive, prices eventually dropped significantly and they came to be widely used in the petrochemical industry, not only for research and development and quality control, but also for process management.

2.4.4 Polymer molding technology

Natural rubber molding technology as a polymer molding technology developed from the mid-19th century onwards. Vulcanization was discovered in 1839. The development of rubber processing machinery and vulcanization techniques (1849) by Thomas Hancock in the United Kingdom significantly advanced rubber molding technology. Although natural rubber is a difficult material to process, molding was achieved with calender molding technology using rollers, and through press molding technology. In the 20th century, rubber molding technology had become a large-scale industry before the Second World War, with many rubber molding products being used in the automotive industry, such as for car tires. Natural rubber molding in Japan started in 1886, when Tsuchiya Rubber Factory commenced operations using vulcanization methods. The tire industry became established in Japan in the 1920s, and by 1931 Bridgestone had commenced production of a purely Japanese-produced tire.

Meanwhile, celluloid, a thermoplastic polymer, was industrialized in the late 19th century and was being used in molding products. Natural rubber molding technology was applied to celluloid molding. In the 1910s, phenol resin, a thermosetting resin, was industrialized. The molding method was compression molding, an extension of press molding. By the 1930s, polyvinyl chloride, polystyrene, polyethylene and other polymers had been industrialized in Europe. While the molding of these polymers did not extend beyond applying rubber molding technology, the screw extruder soon emerged as what could be called an archetype for modern extruders. By 1939, hard PVC pipes were being manufactured in Europe.

Highly productive molding technologies for thermoplastics include extrusion molding, blow molding and injection molding. Injection molding had been developed in the West before the Second World War, but only for very small products at very slow speeds. In the 1950s, Japan made significant advances in PVC, polyvinyl acetate (PVA) and urea resins through coal chemistry. Japan was also importing polyethylene and polystyrene. Molding fabricators and molding machine companies started out by importing molding machines from the West and starting to produce molding products. Right around this time there were some rapid developments in extrusion molding and injection molding, making it possible to produce larger products faster. Accordingly, in the late 1950s, just as the petrochemical industry was being established in Japan, a foundation was being laid for new plastic molding. After that, petrochemistry and plastic molding technology started developing through mutual interaction, a trend that has continued to the present day.

A similar thing occurred with synthetic fibers. The rayon industry, which had seen major developments in Japan since the 1920s, used a wet spinning method in which the polymers were dissolved in a solvent and then spun. This was because cellulose, the feedstock for rayon, is not a thermoplastic polymer. By contrast, nylon, industrialized in the United States at the end of the 1930s, used a process called melt spinning, since it is a thermoplastic polymer. Even Japan started small-scale production of nylon during the Second World War using domestic technology, and was able to produce it using melt spinning. Melt spinning was applied to polyester fiber as well in the late 1950s, leading to a series of technological innovations from the 1970s onwards, such as continuous polymerization and spinning, and integration of high-speed spinning, drawing and false-twist texturing.

2.5 Petrochemical technology characteristics

While there are of course many exceptions, a comparison with mass-producing chemical industries that predated petrochemistry and present-day non-petrochemistry chemical industries reveals the five major distinguishing characteristics of petrochemical technology shown in Fig. 2.7.

2.5.1 Part of energy revolution

In the 1950s, oil from the Middle East started being supplied in large volumes to Japan and Europe, and the main source of energy switched to petroleum from coal, which had been in constant use since the Industrial Revolution of the 18th century. This era was known as energy revolution. Chemical industries that used coal and agricultural produce for feedstocks also started switching to petroleum as a feedstock. This was part of energy revolution.

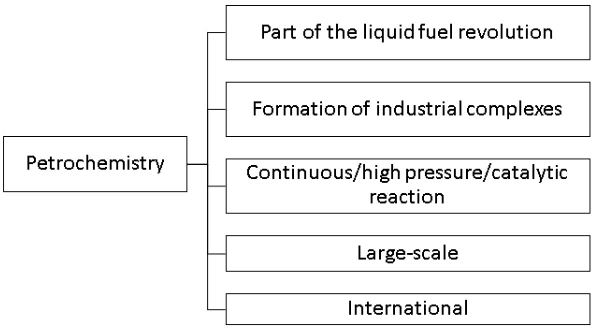

Fig. 2.7 Petrochemical technology characteristics.

One significant characteristic of petrochemistry is not only using petroleum as a feedstock, but also using it in fluid form as much as possible at each stage of petrochemical product production. Basic petrochemicals and many industrial organic chemicals exist in gas or liquid form at normal temperatures. Therefore, they are often transported within factories by pumps and pipes, and often stored in tanks. One of the biggest reasons for amalgamating petrochemical factories together and forming petrochemical industrial complexes is that this makes it easier to handle fluid substances. Long-haul transportation between factories is also often done on a large scale by tank trucks, railroad tank cars or tankers, thereby making best use of the fluid properties.

By contrast, polymers are often solid products, although some are liquids, such as solvents and emulsions. However, these solids are often handled in grain form, such as powders or pellets.

2.5.2 *Kombinats* or industrial complexes

In petrochemistry, several basic petrochemical products are co-produced, and then used to produce industrial organic chemicals and polymer products. As mentioned above, basic petrochemical products and many industrial organic chemicals are fluids. Therefore, the factories are converged together and connected with pipes for transporting products or raw materials, thus forming *kombinats* or industrial complexes [Footnote 9].

In many cases in Japan, industrial

[Footnote 9] As mentioned in Footnote 8, there were instances of industrial complexes forming in coal chemistry and electrochemistry. However, it is standard practice in petrochemistry to form industrial complexes; petrochemical industrial complexes are also far larger in scale.

complexes have formed as industrial organic chemical plants and polymer plants have gathered around naphtha steam-cracking plants. Most industrial complexes are not connected to each other and instances of versatility between basic petrochemical products such as ethylene or propylene through pipes are rare. Although the situation in Europe is essentially similar to Japan, there are long-distance ethylene pipelines across the continent, and some industrial complexes even link to other industrial organic chemical plants and polymer plants. The United States has a long-distance pipeline network for ethylene and other products; many ethane or naphtha steam-cracking plants are connected into this network. Many industrial organic chemical plants and polymer plants are also connected into this network. This situation is referred to as a “spaghetti bowl.”

2.5.3 Continuous, high-pressure, catalytic

Factory layout and operational methods in the chemical industries vary significantly depending on whether a chemical reaction takes places continuously or in batches. Many reactions in petrochemistry are continuous, with distillation and other processes also carried out continuously. Operations are also carried out continuously. Under the provisions of the old *High Pressure Gas Control Act* and other such laws, naphtha steam-cracking plants in Japan would close once a year for maintenance, but operate continuously at all other times. At the present time, the regulations have eased up, and plants can now operate continuously for several years at a time. Many industrial organic chemical plants and polymer plants also operate continuously and carry out continuous reactions.

Many petrochemical reactions are also carried out under high pressure, unlike some of the other chemical industries that predate petrochemistry, such as coal tar chemistry, acetylene chemistry and fermentation chemistry. The use of high pressure has often come under criticism from the perspective of energy conservation and been deemed as too much of a contrast from natural conditions, in which reactions are carried out at room temperature and atmospheric pressure. However, the use of moderately high pressure has made a significant contribution to equipment productivity, and is also a means of achieving optimal reaction conditions. Reactions at room temperature and atmospheric pressure are not necessarily categorically superior.

Petrochemical technology can also be categorized by heavy catalyst use, particularly solid catalysts. Advances and improvements in catalysts have been crucial to competition among petrochemical companies. Ironically, ethane and naphtha steam-cracking have the largest plants in petrochemistry and also serve as the foundation for the supply of basic petrochemical products, but are non-catalytic reactions.

2.5.4 Large-scale

Even in the late 1950s, when petrochemical technology was only just introduced to Japan from the West, petrochemical facilities and factories were far larger in scale than those found in coal chemistry and other mass-producing chemical industries. The amount of capital needed to build these large-scale facilities and factories was far more than made sense to any of the other chemical industries. Also, since many of the products were unknown to the Japanese market, there were huge risks for companies aspiring to get into petrochemistry. This was one reason for promoting the formation of corporate groups.

Up-scaling rapidly progressed from the 1950s to the 1960s. With the price of oil dropping, the petrochemical industry proved to have good economy of scale. Naphtha steam-cracking plants that had been built in the late 1950s with 20,000-ton annual ethylene production capabilities rapidly expanded to 50,000-ton capabilities in the early 1960s, to 100,000-ton capabilities in the mid-1960s, and to 300,000-ton capabilities by the end of the 1960s. The speed of expansion slowed after the oil crises; currently, four decades since the 1970s, new ethylene plants are built with annual production capabilities of around 0.6–1.2 million tons (or 1–1.5 million tons for ethane steam-cracking plants, which require less investment expenditure). Industrial organic chemical plants and polymer plants are also increasing in scale. Thus, one of the major distinguishing characteristics of petrochemistry is being far greater in scale than other chemical industries.

2.5.5 Internationality

Since expanding to Europe and Japan from the United States in the 1950s, petrochemistry has been international in its technology, feedstocks and product trading. Neither the synthetic dye industry, which developed in the late 19th century, nor the coal chemical industry, which developed in the 20th century, has had this level of internationality; they have shown strong cartel-like tendencies, rejecting newcomers and trying to hold a monopoly. Technology was an effective means to that end. By contrast, since petrochemistry came after the Second World War amidst a world-wide proliferation of antitrust policies, it has been difficult for anybody to gain a worldwide production monopoly by concealing new petrochemical technologies. The patent agreement between DuPont in the United States and ICI in the United Kingdom was abolished in 1952 due to violation of antitrust laws. In the 1950s, concerned that the dominant American petrochemical companies would expand into Japan and Europe, the Japanese government and various European governments placed strict regulations on capital expansion. This is thought to be another reason that facilitated the internationalization of the technology. Instead of being unable to be leveraged, new technology was licensed to start recovering the expenses of development as soon as possible. British company ICI sent an enquiry commission to Japan in the 1950s specifically to promote the high-pressure polyethylene technology it had developed in the 1930s.

From such beginnings, petrochemical technology continued to become even more internationalized from the 1970s onwards as plant engineering companies expanded.

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3 Petrochemical product categories

The previous chapter provided a bird’s-eye view of the forest that is petrochemistry. Since this does little to reveal any detail, let us now enter that forest. In other words, this chapter discusses petrochemical product categories and how these products are made.

While petrochemical products can be broadly grouped into three categories: basic petrochemical products, industrial organic chemicals and polymers, they are not necessarily always produced in this order. In many cases, polymers are made from basic petrochemical products without first being made into industrial organic chemicals. Since industrial organic chemical products and polymer products are generally made separately according to the number of carbon atoms in the basic petrochemical product, here we shall discuss industrial organic chemicals and polymers together in order of the number of carbon atoms in the basic petrochemical product.

For those who are unfamiliar to chemistry, this chapter may seem to be complicated and confusing. It should suffice to look at only the figures and tables, and to note the magnificence and intricacy of modern petrochemical industries.

3.1 Global petrochemical industries by product categories

Since petrochemical product categories are complex and there is every chance that we would lose sight of the overall forest if were looked too closely at the individual trees, let us first examine the patterns in major petrochemical product categories around the world, thereby revealing the broader categories in the forest that is petrochemistry.

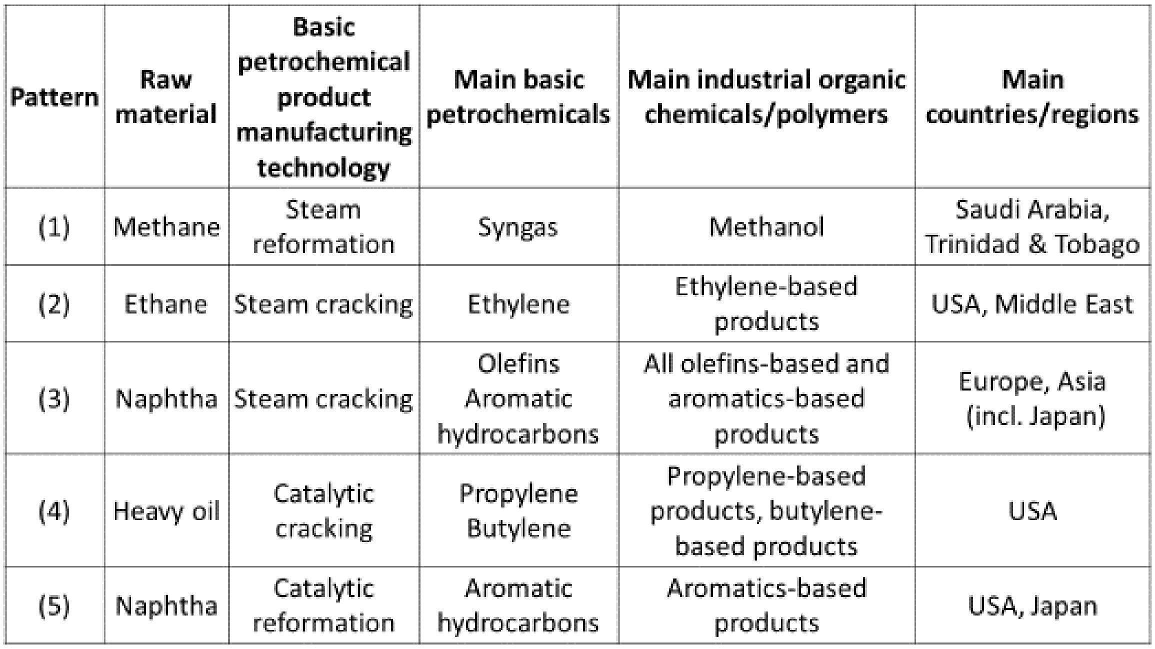
Basic petrochemical product categories largely depend on the raw material used. If the raw material is methane, with C1, then only basic petrochemical products with C1 can be produced. If the raw material is ethane, with C2, then the only basic petrochemical product that can be produced is ethylene, with C2. If the raw material is propane or butane, with C3 or C4, then the main basic petrochemical products produced will be olefins with C2 to C4. If the raw material is naphtha, gas oil or other petroleum product (hydrocarbon mixtures with five or more carbon atoms), then the basic petrochemical products produced will be olefins and aromatic hydrocarbons.

The size and complexity of petrochemical products are determined by the number of carbon atoms in the raw material. The main petrochemical product line patterns around the world can be broadly categorized into five groups, as shown in Table 3.1.

Pattern (1) is the petrochemistry to produce methanol from syngas using natural methane gas as a raw material. At the present time, over 1 million tons of methanol is produced annually at large-scale plants. Although there are several derivative products made from methanol, as shall be mentioned later, very few derivative products are produced on a large scale at methanol production sites. In many cases, methanol is exported in its manufactured form. Accordingly, it is no overstatement to say that Pattern (1) is methanol-plant petrochemistry.

Pattern (2) is the petrochemistry to produce ethylene products from ethylene using ethane from natural gas and associated petroleum gas as raw materials. At present, plants have been built with annual ethylene production capabilities of over 1 million tons; these are in the form of industrial complexes that produce several different types of ethylene-based products using ethylene as a raw material. Pattern (3) is the petrochemistry to produce a lot of different industrial organic chemicals and polymers from a wide variety of olefins and aromatic hydrocarbons using naphtha, gas oil and other liquid petroleum products as raw materials. Since plants are presently being built with ethylene production capabilities of over 500,000 tons (over 1.5 million tons of basic petrochemical products in total), these are taking the form of industrial complexes surrounded by a number of derivative product plants. While Patterns (2) and (3) are in competition on the global ethylene-based products market, non-ethylene-based products are mainly provided through Pattern (3), as Pattern (2) generally produces no non-ethylene-based products.

Table 3.1 Global petrochemical industries by products



Pattern	Raw material	Basic petrochemical product manufacturing technology	Main basic petrochemicals	Main industrial organic chemicals/polymers	Main countries/regions
(1)	Methane	Steam reformation	Syngas	Methanol	Saudi Arabia, Trinidad & Tobago
(2)	Ethane	Steam cracking	Ethylene	Ethylene-based products	USA, Middle East
(3)	Naphtha	Steam cracking	Olefins Aromatic hydrocarbons	All olefins-based and aromatics-based products	Europe, Asia (incl. Japan)
(4)	Heavy oil	Catalytic cracking	Propylene Butylene	Propylene-based products, butylene-based products	USA
(5)	Naphtha	Catalytic reformation	Aromatic hydrocarbons	Aromatics-based products	USA, Japan

Pattern (4) is the petrochemistry to produce propylene-based and butylene-based products from propylene and butylene from byproduct waste gas emitted when producing the gasoline fraction using heavy oil as a raw material. Pattern (5) is the petrochemistry to produce aromatic-based products by extracting aromatic hydrocarbons from reformate. Patterns (4) and (5) only take place in countries and regions where gasoline is produced from heavy oil, or where high-octane gasoline is produced in large volumes. Since the main aim is to produce gasoline, and basic petrochemical products are byproducts, these complement Patterns (2) and (3). In the United States, Pattern (2) is common while Pattern (3) is rare; meanwhile, since there is a high supply from Patterns (4) and (5), these are the main source of supply for non-ethylene-based products.

3.2 Raw materials for petrochemistry

Different petrochemical industries in different countries around the world produce different product categories, due to the different raw materials available. Since raw materials are the greatest determining factor for the petrochemical industry, let us first discuss the raw materials in petrochemistry.

3.2.1 Oil/natural gas producing areas and location of petrochemical industries

The raw materials for petrochemistry are petroleum and natural gas, as previously mentioned. Both are made up of hydrocarbons, and both are extremely useful as sources of fuel (energy). In terms of the overall consumption of petroleum and natural gas, only a very small amount is used as raw materials for petrochemistry. Where natural gas is used as a fuel (energy) source, it is transported long distances in its natural state through pipelines, or converted into liquefied natural gas (LNG) and transported by LNG tankers. Long-distance transportation can be adequately covered by a fixed cost, since far higher quantities of gas are used for fuel than for petrochemical raw materials. However, where natural gas is used as a petrochemical raw material, it is consumed near the production site rather than being transported long distances. By contrast, petroleum is often transported near to the area of consumption, since crude oil and even naphtha, the main petrochemical raw material, can be transported long distances in large tankers.

Consequently, in areas with natural gas, petrochemical industries tend to be located near production sites. In areas without natural gas, imported crude oil, naphtha and other petroleum products are used as raw materials, and petrochemical industries have developed near areas of consumption.

3.2.2 Natural gas

Most of the natural gas mined in the North Sea, Russia, Asia and the Pacific, including the small amount mined in Japan, is made up of only methane. Methane is the simplest saturated hydrocarbon with C1 [Footnote 1]. In Japan, methane is imported long-haul in large quantities in LNG form; it is solely used as fuel for thermal power generation and city gas supplies. Since it can be expensive, it is rarely used as a petrochemical raw material. Petrochemical and ammonia/fertilizer industries that use methane as a raw material are often located near methane production sites. Many of the world’s natural gas fields are in remote locations that are of little use, as the methane cannot be transported anywhere.

While natural gas mined in the United States, Canada and the Middle East is mainly made up of methane, it can also contain a percentage of ethane, a saturated hydrocarbon with C2, as well as a small proportion of propane and butane, saturated hydrocarbons with C3 or C4. The same is true of shale gas mined in the United States, a recent topic of discussion. Ethane, propane and butane can be cracked and used as raw materials for olefins. As propane and butane are easily liquefied, they are often made into liquefied petroleum gas (LPG) and transported long distances to be sold for fuel. Since ethane is not as easily liquefied as propane and butane, it is used almost solely as a petrochemical raw material near production sites, like methane. If there are no nearby petrochemical facilities, ethane can also be used in fuel without being separated from methane.

3.2.3 Associated petroleum gas

Gaseous hydrocarbons dissolve into crude oil at high pressure underground, but they naturally separate out again at atmospheric pressure when the crude oil is mined. This is called associated petroleum gas. Associated petroleum gas often contains ethane, propane and butane, as well as methane. Once the ethane is separated and recovered, it is used as a raw material for ethylene. The petrochemical industries that have developed in the Middle East on a large scale since the 1980s used associated petroleum gas as a raw material, where previously it had not been used for anything. Associated petroleum gas also contains hydrocarbons that liquefy at atmospheric pressure, corresponding to the naphtha fraction. This is called gas condensate, or natural gasoline. With simple distillation, gas condensate makes an extremely good petrochemical raw material, which is marketed as naphtha, like that distilled from crude oil.

3.2.4 Crude oil and petroleum products

Hydrocarbons with five or more carbon atoms exist in liquid form at atmospheric pressure. Crude oil comes in various forms, depending on where it is produced; some forms are mainly made up of saturated hydrocarbons, while some forms contain high amounts of alicyclic hydrocarbons [Footnote 2] or aromatic hydrocarbons. Crude oil also contains sulfur, nitrogen or other organic compounds. Oil refining industries distill and refine crude oil, separating out different products according to their boiling points: the naphtha/gasoline fraction [Footnote 3], the kerosene/jet fuel fraction, the diesel oil fraction and the heavy oil fraction. Oil refineries also produce various types of complementary petroleum products in the required quantities through various physical treatments and chemical processes, such as vacuum distillation, hydrocracking,

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[Footnote 1] Hydrocarbons made up of carbon chains with only single bonds are called saturated hydrocarbons. They are also known as paraffins or alkanes. Their molecular formula can be represented as C_nH_{2n+2}. Methane CH_4 has the lowest number of carbon atoms of any saturated hydrocarbon. Saturated hydrocarbons are the least reactive of the hydrocarbons.

[Footnote 2] Hydrocarbons that are made up of only single bonds and have a cyclic structure are called alicyclic hydrocarbons. Also called naphthenes or cycloparaffins.

[Footnote 3] The oil fraction with a boiling point between 30–180˚C (or 200˚C) is called naphtha. Naphtha, also called crude gasoline, is mainly made up of hydrocarbons with C5–C12. Gasoline is a type of naphtha used as automotive fuel, with its octane number, sulfur content and benzene content adjusted to particular standards.

thermal cracking, catalytic cracking, catalytic reforming, alkylation, dehydrogenation, hydrotreating, isomerization and caulking processes.

In Japan and other parts of Asia, only naphtha is used as a petrochemical raw material. In Europe, both naphtha and gas oil [Footnote 4] are used as petrochemical raw materials.

Oil refineries produce large amounts of petroleum waste gas during catalytic cracking and other chemical processing. These waste gases are made up of propylene, butylene and other olefins. These olefins can be used as raw materials for petrochemistry as necessary. Catalytic reforming is a type of chemical processing to raise the octane number [Footnote 5] of gasoline. Since catalytic reformate contains high quantities of aromatic hydrocarbons, these can be extracted as necessary to produce basic petrochemical products. Thus, oil refineries often produce and supply basic petrochemicals. Further details on petroleum refining technology have not been included in this report.

3.3 Product categories of basic petrochemicals

Main basic petrochemicals include C1 syngas, C2–C5 olefins and C6–C8 aromatic hydrocarbons. The product categories of basic petrochemicals are given below for each raw material and production technique.

3.3.1 C1 basic petrochemicals

Figure 1 shows the product categories of C1 basic petrochemicals made from methane. The main C1 basic petrochemical is syngas. Carbon monoxide (CO), phosgene ($COCl_2$), hydrogen cyanide (HCN) and chroromethanes are also C1 basic petrochemicals.

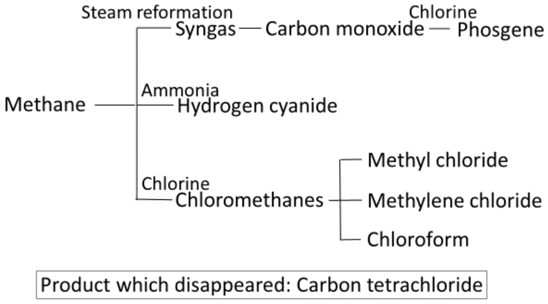

Fig. 3.1 Basic petrochemicals from methane.

Syngas is a mixture of carbon monoxide and hydrogen. It can be made from coal, natural gas and petroleum and also from carbohydrates, though in small quantities. In the petrochemical industry, it is entirely made from natural gas (methane). Syngas thus obtained is further chemically treated to change the carbon monoxide/hydrogen ratio depending on the expected use and is used for synthesis of methanol and production of carbon monoxide. As a raw material for oxo process (hydroformylation), syngas is also used for production of oxoaldehyde and oxoalcohol. In industries other than petrochemistry, it is used for production of hydrogen and synthesis of ammonia and artificial petroleum.

Syngas is manufactured from methane by steam reforming. Methane is reacted with water to give syngas composed of carbon monoxide and hydrogen that is 3 times the volume of carbon monoxide.

C1 basic petrochemicals other than syngas are described below. Carbon monoxide is produced from syngas. Phosgene ($COCl_2$) is made by the reaction of carbon monoxide and chlorine. According to the Andrussow process, hydrogen cyanide is synthesized from methane, ammonia and air at 1,000°C. Water is obtained as a byproduct. According to a modification of the Andrussow process, hydrogen cyanide and hydrogen are only made from ammonia and methane at 1,400°C in the absence of air. Because hydrogen cyanide is produced in large quantities as a byproduct when acrylonitrile is made by ammoxidation of propylene, this process has been used to supply of hydrogen cyanide at a low price since the 1960s. However, owing to improvement of catalysts for ammoxidation

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[Footnote 4] Gas oil is generally the same thing as diesel oil. However, in some cases, gas oil refers to both kerosene and diesel oil.

[Footnote 5] Octane number is an index that indicates the anti-knocking capacity of gasoline engine fuels. The reference criteria range from 0 to 100, with iso-octane having an octane number of 100, and n-heptane having an octane number of 0.

in recent years, the production of hydrogen cyanide as a byproduct has been markedly decreasing.

Chloromethane is made by direct chlorination of methane. It is classified into four types, which are methyl chloride, dichloromethane (methylene chloride), chloroform and carbon tetrachloride, depending on the number of chlorine atoms. If another manufacturing process is used, methyl chloride is made from methanol and hydrogen chloride by dehydration, and is then chlorinated to produce chloromethanes with more chlorine atoms. If this process is used, the necessary products can easily be obtained with a higher yield.

The commercial value of carbon tetrachloride was lost in the 1990s when it was specified as an ozone layer depleting substance and its production and consumption were regulated by the Montreal Protocol. The commercial values of fluorocarbons (such as hydrogen-free chlorofluoromethanes) and halons (such as hydrogen-free bromofluoromethanes) made from chloromethanes have also been lost, because these substances were also classified as ozone layer depleting substances. Fluorocarbon substitutes made from chloroform, etc. are also being regulated one by one to prevent global warming.

3.3.2 Basic petrochemicals from steam cracking of gaseous hydrocarbons

Ethylene and hydrogen are only produced by steam cracking of ethane that is separated from natural gas, crude oil associated gas, etc. Other olefins or aromatic hydrocarbons are rarely produced. In the United States, steam cracking of a mixture of ethane and propane or a mixture of propane and butane is also performed, though on a small scale. In this case, not only ethylene but also olefins such as propylene and butylene are obtained. The production of aromatic hydrocarbons is low. As the steam cracking technique for gaseous hydrocarbons is the same as that for naphtha and gas oil, it is described in the following section.

3.3.3 Basic petrochemicals from steam cracking of liquid hydrocarbons

As shown in Fig. 3.2, liquid hydrocarbons are steam-cracked to give mixtures of olefins and aromatic hydrocarbons as co-products.

(1) Steam cracking technique

Hydrocarbon is cracked when naphtha or gas oil is mixed with superheated steam and is then passed for a few milliseconds through a pipe that is heated above 1,000°C from the outside. The cracked gas is quenched to approximately 300°C in a heat exchanger (quench cooler). As the reaction temperature of steam cracking is 800–900°C, heat can be recovered as high-pressure steam using the quench cooler. The cracked gas is then sprayed with oil (mainly cracked gasoline, mentioned below) in the quench tower and then with water in the next quench tower. As a result, the steam mixed at the time of reaction changes to water, and the C5–C9 fractions of the cracked products are condensed/separated and collected as a liquid (cracked gasoline). Further separation and purification of the cracked product are described in the next section.

Steam cracking described here is not a reaction of hydrocarbons with steam as was mentioned in the preceding section on manufacture of syngas (steam reforming). Steam only lowers the partial pressure of gaseous hydrocarbons. Steam cracking achieved by thermal cracking in the absence of a catalyst is markedly endothermic. Cutting of carbon chains, isomerization, cyclization and dehydrogenation of hydrocarbons occur during the reaction. If the retention time of hydrocarbons is too long, thermal cracking will progress further, ultimately resulting in cracking into carbon and hydrogen. Therefore, the retention time is shortened to avoid this problem, but carbon as a byproduct of hydrocarbon thermal cracking still accumulates in the pipes during operation. Since steam cracking devices are composed of up to a dozen furnaces, the furnace in which the carbon accumulates in the pipes is separated after the supply of raw materials is stopped, and then air is supplied to remove the carbon by combustion. After this decoking operation, the furnace is put into operation again.

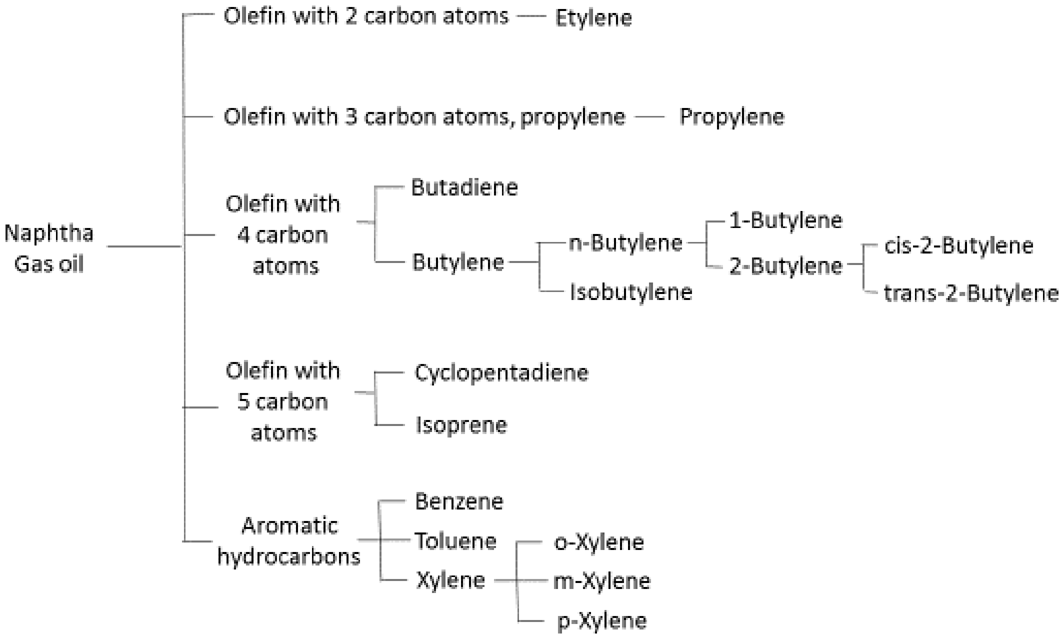

Fig. 3.2 Major basic petrochemicals obtained from steam cracking of naphtha or gas oil.

The production of olefins is higher when the cracking temperature is higher, retention time is shorter, and partial pressure of hydrocarbons is lower (mixed with more steam). Recently, because the main suppliers of aromatic hydrocarbons as a basic petrochemical have also transitioned to oil refiners (catalytic reformate) in Japan, steam cracking devices for naphtha tend to be operated in such a way to obtain more olefins.

The yields of basic petrochemicals produced by steam cracking differ greatly depending on the raw material and conditions for cracking. If the raw material is ethane as mentioned in the preceding section, the yields of ethylene and hydrogen/methane are approximately 80% and 14%, respectively. If the raw material is butane as mentioned in the preceding section, the yields of ethylene, propylene, butylene/butadiene and hydrogen/methane are approximately 38%, 15%, 10% and 25%, respectively. In contrast, if the raw material is naphtha, the yields of ethylene, propylene, butylene/butadiene, basic petrochemicals with five or more carbon atoms (including aromatic hydrocarbons) and hydrogen/methane are approximately 30–35%, 15–17%, 9–12%, 25% and 14–16%, respectively.

(2) Separation and purification of olefins and aromatic hydrocarbons

Since many olefins and hydrocarbons are produced simultaneously during steam cracking of naphtha and gas oil, the techniques for separating and purifying them have progressed. Several separation/purification processes have been developed depending on the order of product separation. Detailed description of each process is avoided here, and how to separate and purify co-products is described below by showing an example.

At first, the cracked product cooled to room temperature in the water quench tower is divided three ways, namely, water, a gas component and a component that occurs as a liquid at room temperature (cracked gasoline).

The gas component is washed with a solution of sodium hydroxide to remove carbon dioxide and traces of sulfur compounds. After drying, the gas is cooled under compression. Hydrogen, the C1 fraction and the C2, C3 and C4 fractions are separated one by one while the gas is being passed sequentially through the distillation columns for demethanization, deethanization, depropanization, debutanization, etc. The C2 fraction is further separated into ethylene and ethane in the ethylene column to give ethylene. Ethane is charged again as a raw material into the cracking furnace. The C3 fraction is separated into propane and propylene in the propylene column to give propylene. As it is very difficult to separate propane and propylene by distillation, a distillation column with a large number of plates is needed. To synthesize industrial organic chemicals, propylene is often purified to a chemical grade of approximately 94%. To produce PP, its purity must be further increased to a polymer grade of 99.5% or more.

Separation of the C4 fraction is time-consuming, because it contains many components. As shown in Fig. 3.3, butadiene is separated first by extractive distillation using a polar solvent. Because three kinds of n-butylene [Footnote 6] and isobutylene are contained in raffinate I from which butadiene has been removed, isobutylene with the highest reactivity is changed to tert-butyl alcohol by hydration in the presence of a solid acid catalyst and separated. Tert-butyl alcohol is returned to isobutylene by dehydration. If it is necessary to separate 1-butylene from the remaining raffinate II, it can be separated by extractive distillation or by using a porous solid adsorbent. Raffinate III from which 1-butylene has been removed is a mixture of cis- and trans-2-butylene. This mixture is usually used, without further separation, for manufacture of alkylate gasoline or synthesis of sec-butyl alcohol.

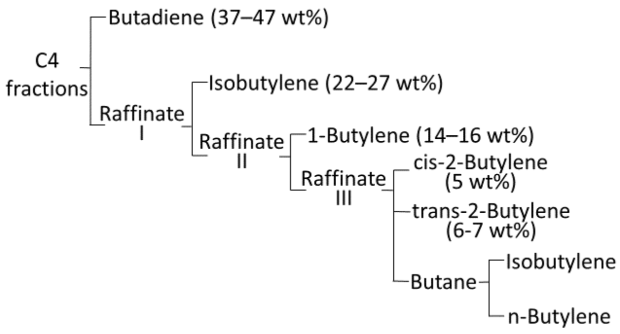

Fig. 3.3 Separation of the C4 fractions.

On the other hand, the C5 fraction is separated first from cracked gasoline which has been separated from the gas component and water in the water quench tower as mentioned at the beginning of this section. Various hydrocarbons are contained in the C5 fraction. However, because it is difficult to separate all of them, only isoprene and cyclopentadiene are separated due to demand. When the C5 fraction is heated at 150°C under pressure, cyclopentadiene is dimerized to give C10 dicyclopentadiene (DCPD) which can be separated by distillation. When C10 dicyclopentadiene is heated at 350°C after separation, cyclopentadiene is reproduced. The C5 fraction from which cyclopentadiene has been separated is subjected to extractive distillation with acetonitrile or N-methyl pyrrolidone to separate isoprene. The remaining C5 fraction is not separated further, but is polymerized and used as petroleum resin.

Aromatic and non-aromatic hydrocarbons are then separated first from the six or more carbon atoms fractions. For this purpose, solvent extraction is often performed using a solvent such as N-methyl pyrrolidone, N-formylmorpholine or N,N-dimethylformamide (DMF).

Aromatic hydrocarbons are further separated by distillation into benzene, toluene and mixed xylene. Mixed xylene (the C8 aromatic hydrocarbon fraction) is a mixture of ethylbenzene, o-xylene, m-xylene and p-xylene. Since these chemicals cannot be separated by distillation due to having similar boiling points, various methods of separating them have been developed. As the demand for p-xylene is much greater, its separation is the most important. At present, the Parex process developed by Universal Oil Products (UOP) in 1971 is widely used (see Section 6.1.1 (6)).

3.3.4 Basic petrochemicals from catalytic cracking and catalytic reforming

In the oil refinery industry, catalytic cracking of the heavy oil fraction is performed to obtain more gasoline fraction as well as the fraction contained in crude oil, resulting in the formation of large quantities

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[Footnote 6] Molecules with a straight carbon chain are called linear molecules, and n is attached. In the case of butylene, 1-butylene, cis-2-butylene and trans-2-butylene shown in Fig. 2.2 are linear molecules.

of waste gas. Since olefins such as propylene and butylene are contained in the waste gas, it is possible to separate/purify and use them as necessary. However, this process is not efficient, because the concentrations of propylene and butylene in waste gas are lower for catalytic cracking of heavy oil than for steam cracking of naphtha. In countries where steam cracking of naphtha is actively carried out, there is low dependence on propylene and butylene separated from waste gas from catalytic cracking, because the production of propylene and of butylene from steam cracking of naphtha correspond to approximately one-half and one-third of the production of ethylene, respectively. On the other hand, in the United States, catalytic cracking of petroleum is performed on a large scale (Section 3.1). When the C3 fraction from catalytic cracked gas is used for synthesis of alkylate gasoline, etc. in the oil refinery industry, it is not distilled precisely but to a refinery grade (approximately 70% propylene purity) (the main impurity is propane with low reactivity). When it is used for production of industrial organic chemicals and polymers, it must be purified to a chemical or polymer grade as mentioned above.

In the oil refining industry, catalytic reforming of naphtha/gasoline fractions is performed to enhance the octane number of gasoline. It is enhanced because hydrocarbon molecules are branced, cyclized and aromatized by catalytic reforming. As a result, aromatic hydrocarbons are contained in catalytic reformates. However, because concentrations of aromatic hydrocarbons are lower for catalytic reformates than for cracked gasoline, various solvent extraction methods have been developed. Old well-known methods are the Udex process (extracting solvent: ethylene glycols/water) developed by UOP-Dow Chemical in 1952 and the sulfolane process developed by Shell-UOP in 1959. On the other hand, new processes using new solvents have also been developed one after another. Catalytic reformates are the main supply source of aromatic hydrocarbons in the United States In places like Europe and Japan, where steam cracking of naphtha is actively carried out, aromatic hydrocarbons can be supplied from cracked gasoline. However, because the demand for aromatic hydrocarbons has increased, the main supply source of aromatic hydrocarbons in Japan has also changed from cracked gasoline to catalytic reformates.

3.3.5 Disproportionation and isomerization of aromatic hydrocarbons

Production of benzene and xylene by disproportionation of toluene and production of mixed xylene by isomerization of m-xylene are included in the techniques of manufacturing basic petrochemicals (see Section 6.1.1 (6)).

3.4 Product categories of industrial organic chemicals and polymers

In the petrochemical industry, industrial organic chemicals and polymers are made from basic petrochemicals according to the number of carbons, and different industrial organic chemicals and polymers are made from individual industrial organic chemicals. Therefore, in this section, the product categories of industrial organic chemicals and polymers are described for each carbon number found among basic petrochemicals.

There are usually several competitive routes and techniques for manufacture of industrial organic chemicals. Moreover, historically, they have often shown profound changes. In this section, typical routes and techniques are described to provide further insight on the product categories of current petrochemistry. Competitive routes and historical changes are explained later.

As there are much more industrial organic chemicals and polymers than basic petrochemicals in the petrochemical industry, it is impossible to describe all of them. Since the purpose of this report is to take a general view of petrochemical manufacturing techniques and to consider the systematization of such techniques, only the typical products manufactured in large quantities worldwide or in Japan are described below.

3.4.1 Product categories from the C1

fraction

C1 basic petrochemicals include syngas, carbon monoxide, phosgene, hydrogen cyanide and chloromethanes. Figure 3.4 shows the categories of main industrial organic chemicals and polymers manufactured from each of them.

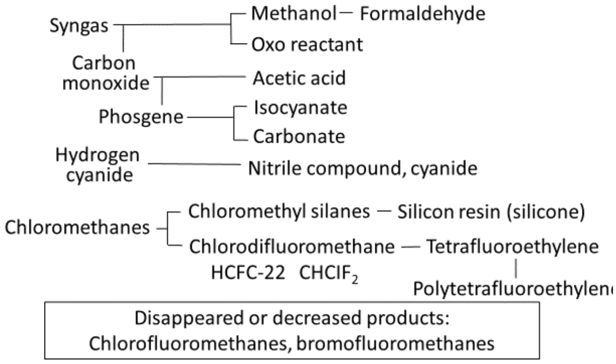

Fig. 3.4 Major product categories from basic petrochemicals with C1.

(1) Methanol

The production of methanol from syngas is greater than that of any other C1 petrochemicals. Methanol is made by the reaction of syngas as a mixture of carbon monoxide and hydrogen at a gas volume ratio of 1:2. . Methanol is used not only as a solvent but also in large quantities for synthesizing industrial organic chemicals. It is used for manufacture of various methyl esters as well as formaldehyde and acetic acid. In recent years, methanol has also been used in large quantities for synthesizing fuels and fuel additives, such as biodiesel oil from fats and oils [Footnote 7] and dimethyl ether.

Formaldehyde is made by dehydrogenation or oxidative dehydrogenation of methanol. Many industrialized processes are available. Formaldehyde is also used for production of phenol, urea and melamine resins. It is used for producing polyacetal as one of the engineering plastics. It is also used as an organic intermediate for making various organic compounds. Pentaerythritol (tetrahydric alcohol), trimethylol propane (trihydric alcohol) and neopentyl glycol (dihydric alcohol) are made by aldol condensation and reduction reaction of formaldehyde with various aldehydes. These alcohols are used as raw materials for unsaturated polyester and alkyd resin and as raw materials for polyether polyol used in polyurethane. Formaldehyde is also used for synthesizing 4,4-diaminodiphenyl methane as a raw material for methylene diphenyl diisocyanate (MDI).

At present, acetic acid is manufactured mainly from methanol and carbon monoxide. This process is explained under (3) in this section.

(2) Oxoaldehyde and oxoalcohol

Aldehydes are synthesized by the oxo process (hydroformylation) in which olefins, etc. are reacted with carbon monoxide and hydrogen. Aldehydes thus obtained have one more carbon atom than the original olefins.

Synthesis of n-butyraldehyde and isobutyraldehyde from propylene is the greatest use of the oxo process. This reaction is also used for synthesis of propionaldehyde from ethylene and for synthesis of β-hydroxypropionaldehyde from ethylene oxide. Propionaldehyde and β-hydroxypropionaldehyde are reduced with hydrogen to give n-propylalcohol and 1,3-propanediol, respectively. Linear higher alcohols are made by the oxo process of α-olefins. Such a series of aldehydes produced by the oxo process are called oxoaldehydes, while alcohols formed by reduction of these oxoaldehydes are called oxo alcohols.

(3) Industrial organic chemicals from carbon monoxide

The most significant industrial organic chemical from carbon monoxide is acetic acid. It is produced by the reaction of methanol and carbon monoxide. The most important use of acetic acid is vinyl acetate. Acetic acid is also used as a solvent for manufacture of terephthalic acid. Acetic acid is also used for other purposes such as the production of acetate, acetic anhydride and chloroacetic acid.

Ube Industries has industrialized a method of co-producing dimethyl carbonate

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[Footnote 7] Biodiesel oil is a higher fatty acid methyl ester. Higher fatty acid methyl esters and glycerin are produced by transesterification between oils/fats (triglycerides as higher fatty acids) and methanol. As the oils and fats, palm oil, rape seed oil and sunflower oil are often used. Biodiesel oil can also be made from used edible oil, though in very small quantities.

and dimethyl oxalate by the reaction of carbon monoxide with methyl nitrite in the presence of a platinum-group metal catalyst (nitrite process). Methyl nitrite is synthesized from nitrogen monoxide, methanol and oxygen. Oxalic acid is obtained from dimethyl oxalate. Ethylene glycol (EG) is obtained by hydrogen reduction of dimethyl oxalate. Accordingly, C2 industrial organic chemicals (oxalic acid and EG) can be obtained from C1 petrochemicals such as carbon monoxide and methanol by the nitrite process (see Section 6.2.3).

(4) Products from phosgene

Phosgene is a highly reactive gas and is used in large quantities for the manufacture of diisocyanate as raw materials of polyurethane and polycarbonate.

Isocyanate is synthesized by the reaction of amine with phosgene. Aromatic diisocyanates (MDI and toluene diisocyanate [TDI]) are produced on a large scale. Of the aliphatic diisocyanates, hexamethylene diisocyanate, isophorone diisocyanate, etc. are not produced on such a large scale, but are essential for the manufacture of non-yellowing polyurethane foam.

Phosgene is reacted with compounds having hydroxy groups to give carbonic acid esters (carbonates). Of these, bisphenol A (BPA) is reacted with phosgene to give large quantities of polycarbonate as an engineering plastic.

Phosgene is also reacted with carboxylic acid to give acid chlorides. As monoisocyanate and acid chlorides are highly reactive industrial organic chemicals, they are used as organic intermediates for the manufacture of pesticides, pharmaceuticals and surfactants.

(5) Industrial organic chemicals from hydrogen cyanide

Alkali salts (sodium cyanide and potassium cyanide) of hydrogen cyanide (hydrocyanic acid) are used in the metal refining, plating and inorganic chemical industries. These substances are also used for introducing a cyano group in organic synthetic reactions and as organic intermediates for dyes, feed additives, pharmaceuticals, pesticides, etc.

Hydrogen cyanide used to be obtained in large quantities as a byproduct of acrylonitrile. At that time, it was reacted with acetone and butadiene to give methyl metacrylate and adiponitrile, respectively. However, in recent years, because the production of hydrogen cyanide as a cheap byproduct has decreased, its large-scale uses have also decreased.

(6) Products from chloromethanes

As industrial organic chemicals from chloromethanes have become regulated as ozone depleting substances or greenhouse gases, the production of these substances has recently decreased to a large extent. However, some important petrochemicals are still being manufactured from chloromethanes.

As a solvent/detergent, dichloromethane (methylene chloride) is widely used not only in the chemical industry but also in the machine industry. Methyl chloride is reacted with silicon to give chlorosilanes. Chlorosilanes are important raw materials of silicone oil, silicone rubber and silicone resin.

Chlorodifluoromethane (HCFC-22) obtained by the reaction of chloroform with anhydrous hydrofluoric acid is thermally cracked to give C2 tetrafluoroethylene. Polytetrafluoroethylene is obtained by radical polymerization of tetrafluoroethylene according to the suspension polymerization method. Polytetrafluoroethylene (PTFE) is a typical fluororesin (Teflon).

3.4.2 Products from the C2 fraction (ethylene-based products)

The C2 basic petrochemical is ethylene. Figure 3.5 shows the categories of main products from ethylene. Of the four major general-purpose resins which are produced in exceptionally large quantities compared with other polymers, polyethylene, polystyrene and vinyl polychloride are made from ethylene. Furthermore, because ethylene is often used as a comonomer of propylene [Footnote 8], it may be said that the products from ethylene including PP play the most

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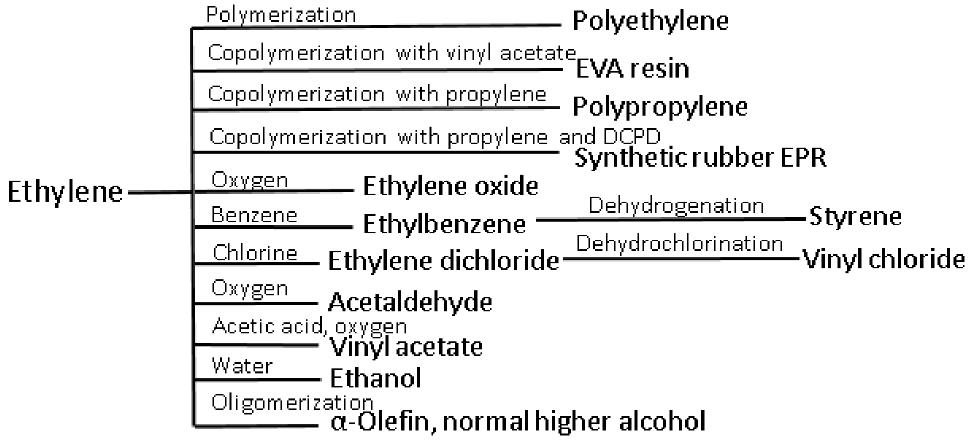
[Footnote 8] Polymers in which only one type of molecule (monomer) is polymerized are called homopolymers. Polymers in which different types of molecule are polymerized (copolymerized) are called copolymers. Of more than one monomer involved in copolymerization, the monomers other than the main monomer are called comonomers.

important role in the petrochemical industry. The reaction of ethylene is mostly addition reaction to double bonds (see Section 6.1.2 (1)).



Other products from ethylene; ethylene wax, triethylaluminum, propionaldehyde, n-propyl alcohol, propionic acid, acetic acid, ethyl acetate, ethyl chloride
Disappeared product : tetraethyl lead, ethylene dibromide,1,1,1-trichloroethane

Fig. 3.5 Major product categories from ethylene.

(1) Polyethylene

Ethylene is polymerized to give polyethylene. Polyethylene is the greatest use of ethylene and is a typical petrochemical that is produced i larger quantities than any other polymers. Since the molecular structure of ethylene is CH_2=CH_2, the basic molecular structure of polyethylene is -(CH_2)-, and thousands to hundreds of thousands of -(CH_2)- are connected. The molecular chain of polyethylene may be almost one-dimensional/straight or branched. Furthermore, in addition to ethylene, a comonomer is used in small quantities to change the performance of polyethylene by slightly modifying the structure of its molecular chain. Thus, as shown in Fig. 3.6, polyethylene is roughly classified into 4 types: low-density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), high-density polyethylene (HDPE) and L-LDPE.

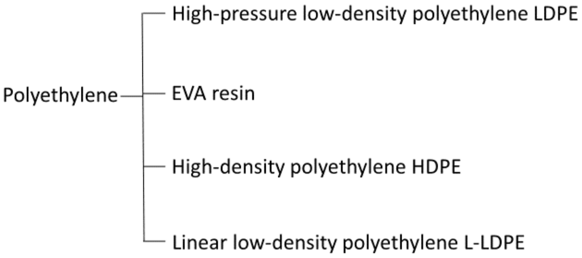


Fig. 3.6 Type of typical polyethylenes.

High-pressure low-density polyethylene (LDPE) is polyethylene that was synthesized for the first time in 1933. LDPE is made by radical polymerization [Footnote 9] at 200°C and 2,000 atm using a trace of oxygen or peroxide as a polymerization initiator [Footnote 10]. The autoclave (vessel) and tubular processes are available depending on the type of reactor, but both of them are based on the bulk polymerization process [Footnote 11]. Because the molecular chain of LDPE is branched substantially,

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[Footnote 9] Chemicals that generate radicals on heating, etc., thus making radical polymerization start are called polymerization initiators. Catalysts do not remain on the molecular chains of polymers, while some of the polymerization initiators become part of molecular chains.

[Footnote 10] Radical polymerization is one of the polymerization reactions. In this reaction, the molecular chain that grows when the polymer chain grows due to the reaction of the monomer is a radical. In contrast, the reaction in which the growing molecular chain is an ion is called ionic polymerization. (See Section 6.1.3 (1) 2), 3))

[Footnote 11] See Secton 6.1.3 (1) for these polymerization method.

crystallization hardly occurs and as a result, it has low density (0.915–0.925) compared with other types of polyethylene. As a transparent flexible film, LDPE is used in large quantities for packaging bags, garbage bags, mulch films for agriculture, etc. It is also used for molded products such as blow-molded bottles and extrusion-molded pipes. Crosslinked LDPE is used as an insulating material for high-voltage transmission line cables. However, because expensive superhigh-pressure facilities are required for LDPE, LDPE has recently tended to be replaced by L-LDPE mentioned below and as a result, there are few new LDPE plants under construction.

Ethylene-vinyl acetate (EVA) resin is a copolymer obtained by copolymerization of ethylene and vinyl acetate. Due to its excellent adhesiveness, it is laminated with other types of polymer film and used as a multilayer film. It is also used as an adhesive (hot-melt adhesive) for paper bags, etc. and as a foamed product for shoes and sandals. EVA resin can be produced using the same manufacturing equipment as for LDPE.

High-density polyethylene (HDPE) is made by ionic polymerization of ethylene [Footnote 10] at room temperature to 250°C and atmospheric pressure to 150 atm. Catalysts are needed for polymerization. By using the Phillips process or Standard Oil of Indiana process depending on the catalyst, polymerization is carried out at a medium pressure of several tens to 150 atm. On the other hand, if a Ziegler or metallocene catalyst is used, polymerization of ethylene can be performed under moderate conditions (atmospheric pressure and less than 90°C). Linear polyethylene without branching can be obtained by both of the medium pressure and atmospheric pressure processes. Since such a molecular chain tends to be folded to produce crystals, slightly higher density (0.955–0.965) translucent polyethylene can be obtained. HDPE does not require the superhigh-pressure manufacturing facilities that are essential for LDPE and consumes much less energy to manufacture than LDPE. HDPE has been manufactured by solution polymerization [Footnote 11] and slurry polymerization [Footnote 11]. However, owing to the development of highly active catalysts, production by gas phase polymerization [Footnote 11] using a fluidized bed reactor started in the 1980s and has subsequently become widely used.

HDPE is often injection- or blow-molded and used for convenience goods, containers, automotive gasoline tanks, kerosene tanks and bottles. HDPE with high molecular weight is extrusion-molded to give an extremely thin but strong film, which is used for disposable shopping bags and packaging bags at supermarkets. As a synthetic fiber, HDPE is used for fishing nets, ropes, filter cloth and insect proof nets. The film is split and extended to give flat yarn and split yarn, which are used for blue sheets, flexible containers, strings for packing, etc.

L-LDPE has low density, while keeping the advantages of HDPE, i.e., low equipment and operational energy costs. When ethylene is copolymerized with a several-percent lower α-olefin such as 1-butylene, 1-hexene or 1-octene [Footnote 12], C2–C6 side chains of alkyl groups occur at random in the molecular chain. Due to such side chains, unlike HDPE, the linear main chain of L-LDPE cannot be changed to crystals, demonstrating characteristics similar to those of LDPE (density, transparency, flexibleness, etc.). Moreover, because highly active catalysts can be used for L-LDPE as well as for HDPE, L-LDPE can also be manufactured by gas phase polymerization with higher productivity. Slurry polymerization is also applicable.

In addition to the four polyethylenes mentioned above, many special polyethylenes and reformed polyethylenes are being manufactured. The molecular weights of the typical polyethylenes mentioned above are approximately 20,000 to 250,000. Polyethylenes of more than 1 million molecular weight are called ultrahigh molecular weight polyethylenes. It is difficult to mold them, but because of excellent abrasion resistance and shock resistance, these polyethylenes are used as engineering plastics. Polyethylene can be crosslinked by

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[Footnote 12] Olefins in which the double bond is at the end of the carbon-carbon bonds are called α-olefins. Both lower α-olefins with a small number of carbon atoms and higher α-olefins with a large number of carbon atoms are available.

exposure to radiation or blending with an organic peroxide during or after molding. Crosslinked polyethylene is clearly more excellent with respect to heat resistance, strength and weather resistance. Various polyethylene copolymers in which ethylene is copolymerized with vinyl compounds are available. Kuraray's EVAL™ is a copolymer of ethylene and vinyl alcohol. Due to its excellent gas barrier properties [Footnote 13], it is used for lamination of packing containers and automotive gasoline tanks. Polyethylene is reacted with chlorine gas, etc. to give chlorinated polyethylene. Since chlorinated polyethylene has the characteristics of both plastic and rubber, it is used as an impact modifier for polyvinyl chloride. As chlorinated polyethylene is resistant to flame owing to the chlorine group, it is also used as a flame retardant for polyethylene and PP.

Ethylene is used for copolymerization with propylene and also for copolymerization of propylene and dicyclopentadiene (DCPD), as shall be described later.

(2) Ethylene oxide

The greatest use of ethylene after polyethylene differs by country. Ethylene oxide, ethylbenzene/styrene and ethylene dichloride/vinyl chloride are almost comparable with respect to the use of ethylene.

Ethylene oxide is manufactured by directly adding oxygen to ethylene in the presence of a silver catalyst. Because carbon dioxide is produced if ethylene is oxidized excessively, selectivity [Footnote 14] is important. To improve selectivity, various attempts have long been made, such as the addition of a small quantity of alkali metal salt as a promoter. As a result, selectivity has improved from around 60% in the 1930s to over 90% at present.

Ethylene oxide is a very reactive gas. It may be used as it is for disinfecting medical apparatus. However, it is usually used for synthesis of industrial organic chemicals and polymers, as shown in Fig. 3.7.

The greatest use of ethylene oxide is ethylene glycol (EG) from a reaction with water. EG is used as an antifreeze for car engines. It is also used in large quantities for the synthesis of polyester (PET resin, polyester fiber and unsaturated polyester resin, etc.). During production of EG, EG obtained is reacted with ethylene oxide to give diethylene glycol, which is then reacted with ethylene oxide to give triethylene glycol. These byproducts are used for solvents and extractive distillation. When more ethylene oxide molecules are polymerized, polyoxyethylene is obtained. Polyoxyethylene with the structure of polymerized EG is also known as polyethylene glycol. Polyoxyethylene is used as a raw material for polyurethane, etc. Since it is nontoxic, it also has prospectice uses in medical devices such as drug delivery systems.

[Footnote 13] Difficulty in passage by gas. Like rubber balloons that deflate on the following day, many polymers tend to let gas pass through when pressurized to a certain extent. Gas barrier property is important performance in food packaging, because difficulty in passage by vapor and oxygen is often required.

[Footnote 14] In chemical reactions, an unexpected substance is often obtained as a byproduct in addition to an expected product. The percentage of reaction producing the expected product is called selectivity.

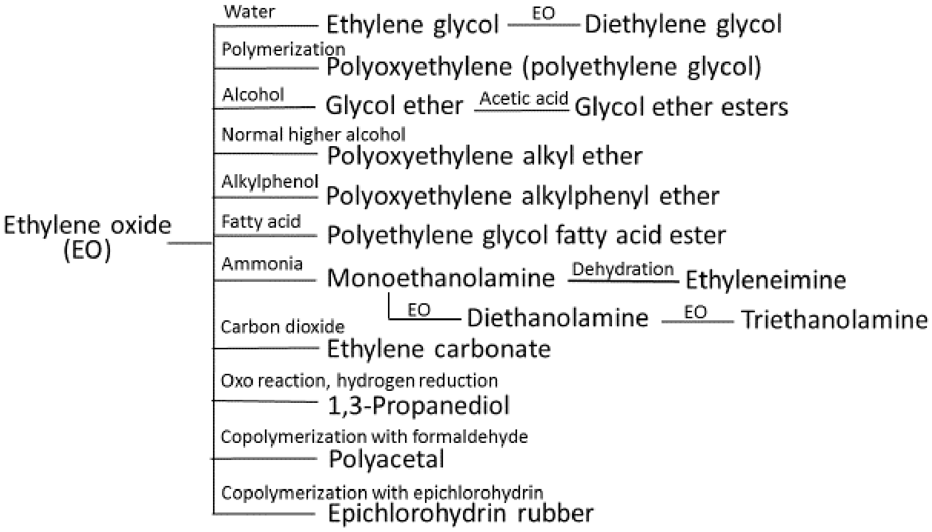

Fig. 3.7 Major product categories from ethylene oxide.

Ethylene oxide is reacted with various lower alcohols to form glycol ethers. Esters with acetic acid are also made by using the hydroxy groups of glycol ethers. Glycol ethers and glycol ether esters are used as solvents for coatings and cleaners.

Since ethylene oxide is reactive to the hydroxy and carboxy groups, it is reacted with linear higher alcohols [Footnote 15], higher fatty acids and alkyl phenol to form a series of compounds to which the polyoxyethylene group -(CH_2CH_2O)n- is added (these products are also known as ethoxylates). Ethoxylates are used for non-ionic surfactants. The polyoxyethylene group is hydrophilic, although it does not dissociate into ions. On the other hand, because the higher alkyl group is lipophilic, ethoxylates are made to nonionic surfactants.

Ethylene oxide is successively reacted with the hydrogen atoms of ammonia to give monoethanolamine, diethanolamine and triethanolamine. As organic intermediates, ethanolamines are used as raw materials of pesticides and pharmaceutical products, as solvents and pH controllers for synthetic detergents and cosmetics and as carbon dioxide absorbents.

Although carbon dioxide is a low-reactivity gas, ethylene oxide is also reacted with carbon dioxide to form ethylene carbonate. Ethylene carbonate is used as a polar solvent, recently attacting attention as an electrolyte for lithium ion secondary batteries. It is also used for the manufacture of polycarbonate in the absence of phosgene.

Carbon monoxide and hydrogen are oxo reacted with ethylene oxide to give 1,3-propanediol in one step via β-hydroxypropionaldehyde (see Section 3.4.1 (2)). Shell industrialized this process in 1999. It has gained attention as a new manufacturing process in contrast with the previous manufacturing process using acrolein (see Section 3.4.3 (8)).

Furthermore, ethylene oxide is copolymerized with formaldehyde to give polyacetal and also with epichlorohydrin to give epichlorohydrin rubber. However, because ethylene oxide is not a main monomer, these polymers are small-scale uses of ethylene oxide.

(3) Ethylbenzene/styrene

Ethylene is reacted with benzene to give ethylbenzene. For this reaction, various acid catalysts and liquid- and gas phase manufacturing processes have been developed. At present, the gas phase process using a zeolite catalyst is usually used in consideration of corrosiveness of facilities, disposal of waste catalysts, recovery of heat, etc. (see Section 6.1.2 (1) 4)). Ethylbenzene is also obtained as one of the C8-fraction chemicals from cracked gasoline produced by steam cracking of naphtha and also from catalytic reformate of petroleum. However,

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[Footnote 15] In organic chemistry, “higher” means that the number of carbon atoms is large, being more than 10, while “lower” means that the number of carbon atoms is small, being 1 to several.

because of the difficulty in separation/purification from xylene, ethylbenzene is mainly synthesized from ethylene and benzene.

Ethylbenzene is mostly used for the manufacture of styrene. It is a typical organic intermediate. Styrene is mainly manufactured by the dehydrogenation of ethylbenzene. Since this reaction is endothermic, like steam cracking of naphtha and ethane, it is performed at 500–600°C while carbonization is prevented by adding high temperature steam to lower the partial pressure. Steam cracking of naphtha and ethane is thermal cracking in the absence of a catalyst, while dehydrogenation of ethylbenzene uses a catalyst. The co-production process of propylene oxide and styrene is also an important route for the supply of styrene (see Section 3.4.3 (4))

As shown in Fig. 3.8, styrene is exclusively used as a raw material for polymers.

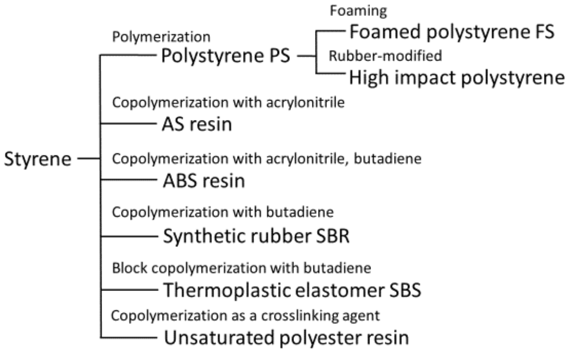


Fig. 3.8 Major product categories from styrene.

Polystyrene as a homopolymer is a hard, transparent polymer. It is made into molded products, sheets and foamed products and used for daily necessaries, electrical appliances, containers, food trays, buffers and heat insulators. To improve the poor impact resistance of polystyrene, high impact polystyrene (HIPS) in which rubber is modified, acrylonitrile-styrene resin (AS resin or styrene acrylonitrile [SAN]) in which acrylonitrile is copolymerized, and ABS resin in which butadiene and acrylonitrile is copolymerized have been developed. ABS resin is not transparent. As colored resin, it is often used for casings of electrical products such as television sets and personal computers. Polystyrene, HIPS, AS resin, ABS resin, etc. are generally known as styrenic polymers.

Another great use of styrene is synthetic rubber from copolymerization with butadiene. Styrene-butadiene rubber (SBR) is a typical synthetic rubber and is used in large quantities for tires. The styrene-butadiene-styrene block copolymer (SBS) is a typical thermoplastic elastomer.

Since various styrene-based polymers are available as mentioned above, bulk polymerization, solution polymerization, suspension polymerization and emulsion polymerization are used on a case-by-case basis. Styrene is also used as a crosslinking agent for processing/molding unsaturated polyesters.

(4) Ethylene dichloride and vinyl chloride

Ethylene dichloride (EDC) is obtained by adding chlorine to ethylene. It is then cracked into vinyl chloride and hydrogen chloride by non-catalytic thermal cracking. The reactants are quenched with cold EDC spray. Hydrogen chloride gas is removed, and vinyl chloride is separated by distillation. This process is very similar to the reactant-quenching process after steam cracking of naphtha. Hydrogen chloride gas is collected and used for ethylene oxychlorination. Ethylene, hydrogen chloride and oxygen or air are reacted by oxychlorination in the presence of a copper chloride catalyst to give EDC and water.

Vinyl chloride is mostly polymerized and used for the production of vinyl polychloride (polyvinyl chloride). Initially, production of vinyl polychloride by radical polymerization was performed by emulsion polymerization using water. However, it was subsequently replaced by suspension polymerization with characteristically good product quality.

As shown in Fig. 3.9, not only polyvinyl chloride but also many industrial organic chemicals are obtained from EDC or vinyl chloride. Vinylidene chloride is obtained when 1,1,2-trichloroethane obtained by chlorination of vinyl chloride is dehydrochlorinated using an alkali. Vinylidene chloride is subjected to radical polymerization to give vinyliden polychloride. Because vinylidene polychloride is excellent in gas barrier property and adhesiveness, it is used as food cling films in daily life.

EDC and chlorine as a raw material gives a mixture of trichloroethylene and tetrachloroethylene. The production ratio of tetrachloroethylene to trichloroethylene can be adjusted by changing the charge-in ratio of EDC to chlorine.

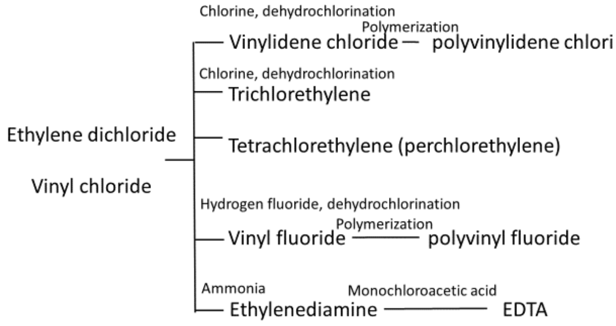


Fig. 3.9 Major product categories from ethylene dichloride, vinyl chloride.

Trichloroethylene is used for solvents and extractive solvents. Tetrachloroethylene, also known as perchloroethylene, is used as a solvent for dry cleaning and a degreasing agent for metal processing. These chlorine-based solvents have the advantage of being flame retardant. However, it is also feared that they could have adverse health and environmental effects. 1,1,1-Trichloroethane as well as tetrachloroethylene, manufactured from vinyl chloride was used in large quantities as a chlorine-based solvent until the early 1990s. However, because it was classified as an ozone depleting substance and its use was regulated by the Montreal Protocol, its production was discontinued in the mid-1990s.

In vinyl fluoride, chlorine of vinyl chloride is replaced by fluorine. Hydrogen fluoride is added to vinyl chloride under pressure in the absence of a catalyst to give 1-chloro-1-fluoroethane, which is then dehydrochlorinated at approximately 500°C to give vinyl fluoride. Vinyl fluoride is exclusively made into vinyl polyfluoride and used as a coating material. It is an industrial organic chemical similar to tetrafluoroethylene obtained from the C1 fraction, although there are clear differences in raw materials and manufacturing processes between the two chemicals.

EDC is reacted with aqueous ammonia under pressure to give ethylenediamine. Ethylenediamine is used as an organic intermediate for the manufacture of pharmaceutical products and rubber chemicals. It is also reacted with monochloroacetic acid to give ethylenediamine tetraacetate (EDTA, edetic acid), which is used as a complex-forming agent.

(5) Acetaldehyde and vinyl acetate

The production scales of other products from ethylene shown in Fig. 3.5 are far smaller than polyethylene, ethylene oxide, ethylbenzene and EDC. However, a great many products are included in this category.

Acetaldehyde as well as vinyl chloride used to be a core industrial organic chemical made from acetylene. Acetaldehyde became a petrochemical product in the latter half of the 1950s when the Hoechst-Wacker process was industrialized (see Section 6.1.2 (2) 1)).. In the presence of a similar catalyst, ethylene, acetic acid and oxygen are reacted to give vinyl acetate.

Acetaldehyde was mainly used for the synthesis of acetic acid, butanol (butyl alcohol) and octyl alcohol. However, in the 1970s, carbonylation of methanol, mentioned previously, was industrialized as a new method of manufacturing acetic acid and was subsequently widely used worldwide. Moreover, the oxo process (hydroformylation) using propylene as a starting material was widely used for manufacture of butanol and octyl alcohol. As a result, acetaldehyde lost its main uses and its production rapidly decreased worldwide from the 1980s onwards. At present, it is only used for the manufacture of small-scale products such as pentaerythritol.

Showa Denko developed a method of manufacturing acetic acid by direct oxidation of ethylene without going through acetaldehyde and industrialized it in the late the 1990s. However, this method has not been widely enough used to replace carbonylation of methanol on a worldwide scale.

Vinyl acetate is polymerized to give polyvinyl acetate (adhesives, coatings and fiber-finishing agents). Polyvinyl acetate is saponified and used for polyvinyl alcohol (paste, coating agents and raw material of polyvinyl butyral). Vinyl acetate is also used as a comonomer for ethylene and vinyl chloride.

(6) Ethanol

Ethanol (also known as ethyl alcohol) is made by adding water to ethylene in the gas phase in the presence of an acid catalyst (phosphoric acid/silica carrier, etc.). Ethanol is widely used as a solvent and is also used as a raw material for ethyl esters such as ethyl acetate. The ethanol market was developed using the fermentation process before the petrochemical industry was established. Afterwards, the petrochemical industry took over the market completely. Therefore, ethanol was the main product of ethylene in the 1950s when the petrochemical industry began to develop rapidly. This was because acetaldehyde could be produced by oxidizing ethanol. However, as it became possible to make acetaldehyde by the Hoechst-Wacker process without first creating ethanol, the commercial value of ethanol began to decline.

(7) α-Olefins and linear higher alcohols

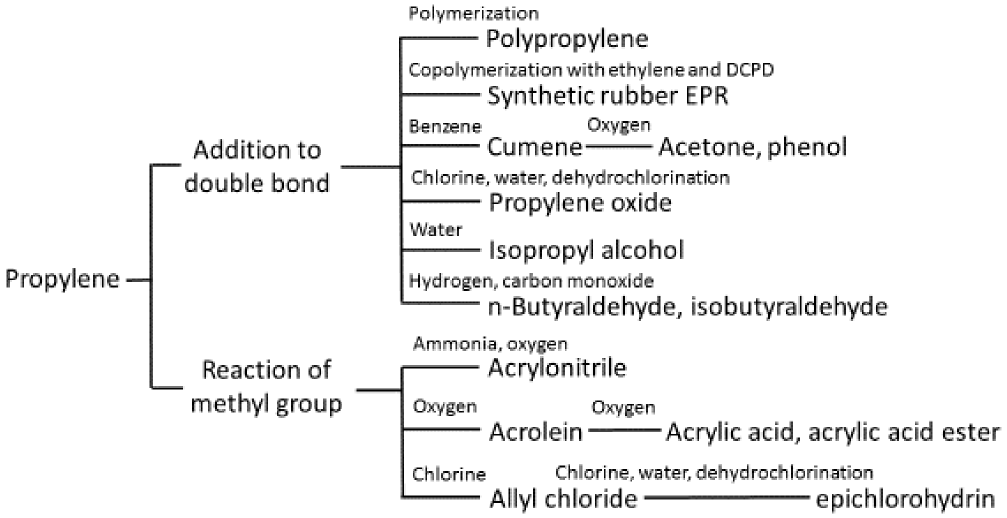
C4 to C20 hydrocarbons with the terminal double bond (at the α-position) are known generally as α-olefins. Among them, C10 to C14 linear α-olefins are particularly important as raw materials for surfactants and lubricants and are being produced industrially. Meanwhile, there has been a growing recent demand for C4 to C8 lower α-olefins for the manufacture of various L-LDPEs.

According to one method of manufacturing α-olefins by oligomerization of ethylene, trialkylaluminium is reacted with ethylene (Ziegler process). This process has been modified and is used even now. However, it has a disadvantage in that the number of carbon atoms of the resulting α-olefin varies considerably from 4 to 24. Linear trialkylammonium is reacted with oxygen and then hydrolyzed to give higher alcohols. When α-olefins are oxo reacted with syngas and then reduced with hydrogen, higher alcohols of odd carbon numbers having one more carbon atom can be obtained.

There is another modification in which the disadvantage of oligomerization of ethylene by trialkylaluminium has been improved to obtain the C6 to C14 olefins that are in great demand. This method has the disadvantage of an increased number of branched chains and internal olefins. The SHOP process developed by Shell and industrialized in 2003 is used for the manufacture of C10 to C14 α-olefins and C11 to C15 higher alcohols with a terminal hydroxy group. α-Olefins with other lengths are reutilized during the reaction.

3.4.3 Products from the C3 fraction (propylene-based products)

The C3 basic petrochemical is propylene. Figure 3.10 shows the main product categories made from propylene. For some time after petroleum chemistry entered full swing in the 1950s, the basic petrochemicals ethylene, butadiene and benzene were in good demand, while production of propylene was greater than its consumption. This was because it was not easy to develop methods of synthesizing C3 industrial organic chemicals (acrylonitrile, acrylic acid, glycerin, etc.) from propylene, although these products had been manufactured in the fields of coal chemistry and oleochemistry since before the establishment of petrochemistry. However, a number of industrial organic chemicals were later developed from propylene. Furthermore, PP was developed and its production increased rapidly, resulting in an increase in the consumption of propylene. Propylene demonstrates two types of reaction, i.e., addition reaction to the double bond, as is observed with ethylene (see Section 6.1.2 (1)), and reaction of the methyl group while leaving the double bond (see Section 6.1.2 (2)). Acrylonitrile, acrolein and allyl chloride are manufactured using the latter reaction.



Products from propylene whose production volume has decreased significantly; propylene oligomers (such as dodecene), glycerin

Fig. 3.10 Major product categories from propylene.

(1) Polypropylene

Unlike ethylene, propylene could not easily be radically or ionically polymerized to obtain an industrial material. It was not until the Ziegler-Natta catalysts were developed in 1957 that polypropylene (PP) could be produced for the first time. Unlike polyethylene, PP has side-chain methyl groups on the main chain of the polymer and therefore in order to obtain an industrial polymer material with good physical properties, propylene must be polymerized in such a way that the side chains are arranged to face a fixed direction. Even the direction of side chains is regulated in stereospecific polymerization, and polymers thus obtained are called stereoregular polymers. All side chains are arranged to face a fixed direction in isotactic polymerization, while in syndiotactic polymerization the side chains are arranged to alternately face different directions. The side chains are not arranged regularly in atactic polymerization.

Since the Ziegler-Natta catalysts are available as fine crystals, polypropylene was initially produced by solution polymerization in which the catalyst was dispersed in a solvent such as hexane and then propylene was passed through the solution. As the activity of the catalyst and the stereoregularity of the resulting polymer were both low, it required decalcification with methanol to remove the catalyst and washing with a solvent to remove low crystalline polymer and low molecular weight polymer after the reaction. As catalysts have improved subsequently, slurry polymerization and mass polymerization (polymerization in liquefied propylene, also known as bulk polymerization) have been developed, making washing and decalcification unnecessary, resulting in a marked reduction in equipment and energy costs. The technology that has dramatically promoted the improvement of catalysts was developed by Mitsui Petrochemical Industries (now Mitsui Chemicals). Japan can boast this polymer synthesizing technoloogy to the world (see Section 5.6.3 (1), Section 6.1.3 (1) 4)).

Meanwhile, a metallocene catalyst that was found as an epoch-making catalyst for polyethylene in the 1980s has also been applied to the polymerization of propylene. Isotactic PP has been the only stereoregular PP that has been produced in the presence of the Ziegler-Natta catalyst. If the metallocen catalyst is used, syndiotactic PP can also be produced. In 2011, Mitsui Chemicals industrialized this process.

As shown in Fig. 3.11, PP is classified as either homopolymer, in which only propylene is polymerized, and copolymer, in which propylene is copolymerized with ethylene.

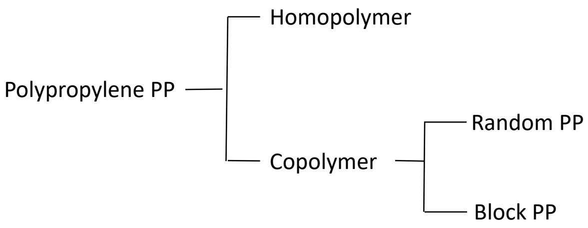


Fig. 3.11 Types of typical polypropylenes.

The copolymer is further classified into random copolymer, in which ethylene is irregularly copolymerized with the propylene sequence by adding a small amount of ethylene (5% or less), and block copolymer (also known as the impact copolymer), in which the propylene homopolymer portion, the random copolymer portion of ethylene and propylene, and the propylene homopolymer portion are connected in that order. The homopolymer is highly crystalline, hard and strong. It demonstrates higher heat resistance than polyethylene and PP random copolymers, and is used for films, sheets, injection-molded products, fibers, unwoven cloth and bands (binding for packaging). Since the crystallinity of the random copolymer is low, its heat-resistance is also low (although it is still higher than the heat resistance of polyethylene). As it can be made transparent and is heat-sealable, it is useful for films and sheets. The film is categorized into nonoriented cast polypropylene (CPP) film and biaxially oriented polypropylene (OPP) film. The random copolymer is also used for injection-molded articles, such as transparent clothes cases and transparent food containers, and blow-molded articles, such as shampoo bottles. The block copolymer is an impact-resistant material characterized by both the hardness and strength of the homopolymer and the flexibility of the random copolymer. It is used for automobiles (car bumpers) and large home electric appliances, having played the most important role in expanding the demand for PP since the 1980s.

(2) Synthetic rubber (EPR)

EPR is a polymer in which ethylene, propylene and an unconjugated diene such as dicyclopentadiene or ethylidene norbornene as the third component are copolymerized in the presence of the Ziegler-Natta catalyst [Footnote 16]. EPR is also known as ethylene propylene diene rubber (EPDM) because it is composed of ethylene, propylene and a diene monomer. EPR that can be vulcanized with sulfur is used as synthetic rubber. Most of the conjugated diene-based synthetic rubbers have double bonds in the main chain of the polymer with unsaturated bonds still remaining in the main chain even after it is partially involved in vulcanization (see Section 3.4.4 (1)). This is the primary cause of the deterioration of rubber on exposure to oxygen/ozone and light. In contrast, the bonds in the main chain of EPR are all saturated, while unsaturated bonds are all in the side chains. Since EPR is outstanding in resistance to weather, heat and chemicals, it is widely used for automotive parts such as tires and tubes.

(3) Cumene, acetone and phenol

Like ethylbenzene, cumene is manufactured by the reaction of propylene and benzene. In the same way that styrene is produced by the dehydrogenation of ethylbenzene, α-methylstyrene can be produced by the dehydrogenation of cumene. α-Methylstyrene is a small-scale industrial organic chemical that is used in small quantities as a comonomer for improving the heat resistance of ABS resin. Since α-methylstyrene is obtained as a byproduct of the co-production of phenol and acetone from cumene as mentioned below, this process is actually the main source of supply of this compound.

The main use of cumene is the co-production of acetone and phenol. Cumene is oxidized with air to give cumene hydroperoxide. Treated with sulfuric acid, the peroxide is cleaved to give phenol and acetone. Since one mol each of acetone and phenol are produced simultaneously from 1 mol of cumene, the balance of demand between acetone and phenol is important. In the past, there was a great demand for acetone, while the supply of phenol tended to be excessive. In that case, acetone could be

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[Footnote 16] Olefines with two double bonds are called dienes. Dienes sandwiching a single bond between two double bonds are called conjugated dienes, while dienes sandwiching two or more single bonds between two double bonds are non-conjugated. Two double bonds react irrespectively of each other in the case of non-conjugated dienes.

supplied by dehydrogenation or oxidative dehydrogenation of isopropyl alcohol, as mentioned below. Conversely, in recent years, there has been a great demand for phenol, while the supply of acetone has tended to be excessive. Using a recently industrialized method, acetone is reduced with hydrogen to give isopropyl alcohol, which is then dehydrated to propylene and returned into a raw material of cumene. However, because a supply of hydrogen is needed, the process is more costly than it would be in the event of an acetone shortage.

As benzene-derived phenol is explained in the "Benzene" section (see Section 3.4.5), only propylene-derived acetone is described in this section. Acetone is important not only as a solvent but also as an organic intermediate, as shown in Fig. 3.12.

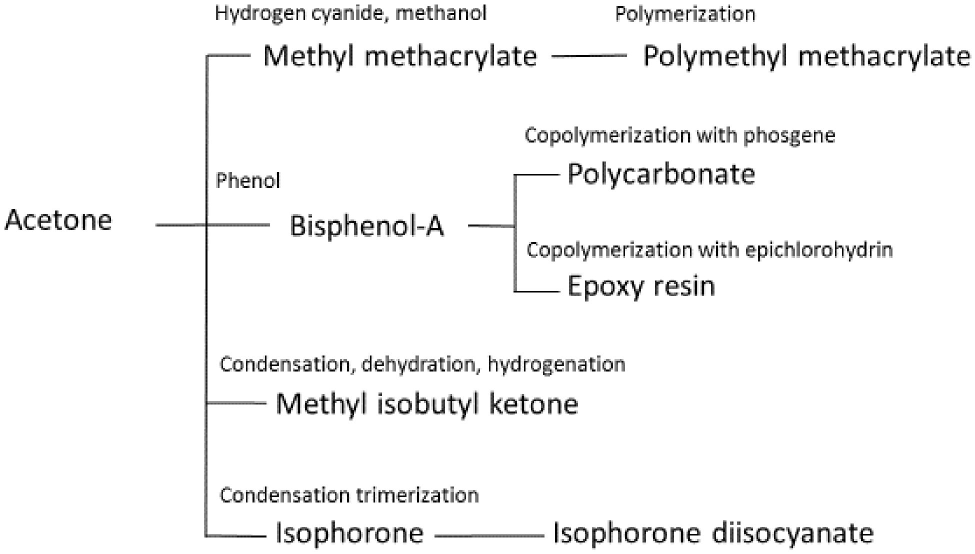

Fig. 3.12 Major product categories from acetone.

At present, the greatest synthetic use of acetone is BPA obtained by reaction with phenol. This substance is also described in the "Benzene" section. The next most important use is methyl methacrylate (MMA) that is synthesized via reaction with hydrogen cyanide. Although for a long time this reaction was the main process of manufacturing MMA, it has rapidly decreased in importance recently. One of the reasons is that the supply of cheap hydrogen cyanide as a byproduct of acrylonitrile has markedly decreased. Another reason is that methods of manufacturing MMA by using C4 isobutylene and tert-butyl alcohol as starting materials have been developed and widely used.

C6 methylisobutyl ketone is obtained by aldol condensation of 2 molecules of acetone followed by several steps of reaction. This compound is used as a solvent. Isophorone is obtained by aldol condensation of 3 acetone molecules. Isophorone is used not only as a high boiling point solvent but also as an organic intermediate. Isophorone diisocyanate is an important organic chemical induced from isophorone. As aliphatic diisocyanate, it is used for the production of polyurethane.

(4) Propylene oxide

Figure 3.13 shows the products from propylene oxide. Compared with Fig. 3.7 showing the product categories from ethylene oxide, the product line-up from propylene oxide is very poor, comprising only propylene glycol, polypropylene glycol and propylene glycol ether, corresponding to EG, polyethylene glycol and glycol ether.

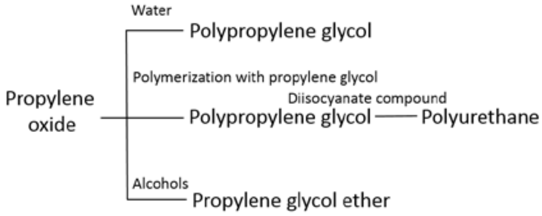

Fig. 3.13 Major product categories from propylene oxide.

Propylene oxide is entirely used for polypropylene glycol as a raw material for polyurethane. Polypropylene glycol, in which polyhydric alcohol is polymerized with propylene oxide, is called polyether polyol. It is used as a raw material for thermosetting polyurethane.

Propylene glycol is used for polyether polyol and unsaturated polyesters. However, it is just one of the polyhydric alcohols such as EG, glycerin and pentaerythritol. Its product scale is much smaller than EG.

Various propylene glycol ethers made from propylene oxide and lower alcohols are solvents that compete with various glycol ethers (cellosolves) made from ethylene oxide and lower alcohols. However, they are not as large-scale.

In the structure of propylene oxide as well as ethylene oxide, oxygen is directly added to the double bond. The direct addition of oxygen to ethylene was achieved in the 1930s, while the direct addition of oxygen to propylene has not yet been achieved. The chlorohydrin process as a very old method of synthesizing ethylene oxide is still used commonly for the production of propylene oxide. As this process is very wasteful, many other manufacturing methods have been investigated.

A method that has been industrialized is the oxidation of propylene with a peroxide to give propylene oxide. If the product obtained after the reaction of the peroxide is useful, the process can be industrialized as a method of manufacturing the product and propylene oxide simultaneously. However, it is difficult to manage co-production, because it is influenced by the supply-demand balances and markets for the two products. Table 3.2 shows the main industrialized peroxides together with their raw materials and products.

Of these methods of manufacturing propylene oxide, process (1) was convenient while MTBE required large quantities of tert-butyl alcohol. However, after the use of MTBE for gasoline was prohibited, there was no demand for tert-butyl alcohol. Process (2) has become a promising route to supply styrene. According to process (3), because cumene and then cumene hydroperoxide can be produced from cumyl alcohol, the product from the peroxide is returned to the original raw material. Thus the disadvantages of co-production can be avoided. Since hydrogen peroxide has recently been produced on a large scale and supplied cheaply, process (4) using hydrogen peroxide as a peroxide has been industrialized. As only propylene oxide and water are produced in this process, the problems of co-production can be completely solved.

Table 3.2 Typical propylene oxide production process by peroxide

	Peroxide	Raw material of peroxide	Product after the reaction of the peroxide
(1)	tert-Butyl hydroperoxide	Isobutane	tert-Butyl alcohol (Dehydrated to isobutylene)
(2)	Ethylbenzene hydroperoxide	Ethylbenzene	Phenyl methyl carbinol (Dehydrated to styrene)
(3)	Cumene hydroperoxide	Cumene	Cumyl alcohol (Dehydration hydrogen reduction to cumene)
(4)	Hydrogen peroxide	Hydrogen	Water

(5) Isopropyl alcohol

In the same way that ethanol is produced by adding water to ethylene, isopropyl alcohol (IPA) is produced by adding water to propylene. Isopropyl alcohol is used as a cheap alternative solvent to ethanol. It used to be an important raw material of acetone. However, as mentioned above, a significant amount of demand for it was lost due to the fact that acetone became excessive in the co-production of acetone and phenol.

(6) n-Butyraldehyde and isobutyraldehyde

n-Butyraldehyde and isobutyraldehyde having one more carbon atom are produced by the oxo process of propylene (see Section 3.4.1 (2)). Figure 3.14 shows the main products from n-butyraldehyde and isobutyraldehyde.

n-Butyraldehyde is condensed with aldol in the presence of an alkali catalyst, dehydrated, and reduced with hydrogen to give 2-ethylhexanol (an octanol). 2-Ethylhexanol is reacted with phthalic anhydride to give dioctyl phthalate (DOP). It is also reacted with adipic acid or phosphoric acid to give esters with a 2-ethylhexyl group. These esters from 2-ethylhexanol are used in large quantities as plasticizers for polyvinyl chloride. n-Butyraldehyde is reduced with hydrogen to give n-butanol. Acrylic acid esters of n-butanol and 2-ethylhexanol are used as raw materials for coatings. Meanwhile, isobutyraldehyde is reduced with hydrogen to give isobutyl alcohol. Both n-butanol and isobutyl alcohol are used as solvents, but n-butanol with higher solubility is more popular as a solvent in coatings. In this way, n-butyraldehyde has a greater demand than isobutyraldehyde

(7) Acrylonitrile

Propylene is reacted with ammonia and oxygen to give acrylonitrile. This reaction, known as ammoxidation, is one of the epoch-making reactions in the technological history of petrochemistry. This reaction is also called the “Sohio process” after the company that invented it. It is significant in that it is not the double bond but the methyl group of propylene is reactive. This reaction was discovered in the latter half of the 1950s. In the 1960s, it replaced many existing methods of manufacturing acrylonitrile, such as the hydrogen cyanide process to give acetylene. Initially, because the the reaction had low selectivity, large quantities of hydrogen cyanide and acetonitrile were produced as byproducts. Hydrogen cyanide was used for many purposes such as methyl methacrylate. Initially, the use of acetonitrile was limited, but the demand for this compound as polar and extracting solvents subsequently gradually expanded. However, due to progressive improvements in catalysts in recent years, the production of these byproducts has decreased. Alternative methods are available for manufacture of hydrogen cyanide, but some measures must be taken for acetonitrile, as it has long been manufactured only as a byproduct of acrylonitrile.

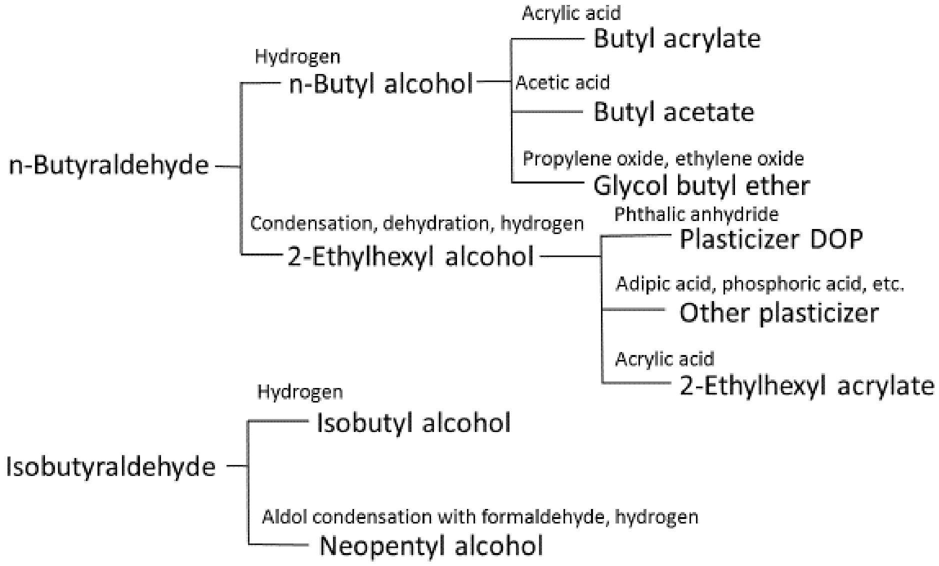

Fig. 3.14 Major product categories from butyraldehyde, isobutyraldehyde.

As shown in Fig. 3.15, acrylonitrile is used for many purposes.

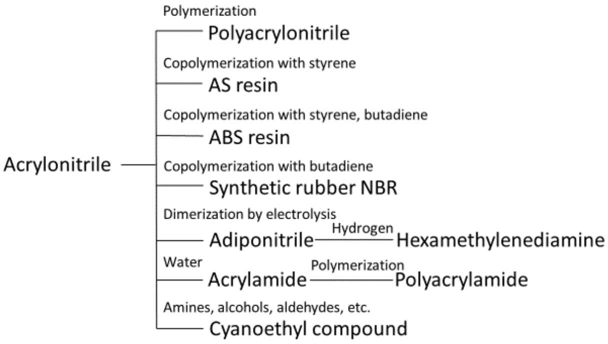

Fig. 3.15 Major product categories from acrylonitrile.

Acrylonitrile is polymerized to give polyacrylonitrile (PAN). PAN is used for acrylic fiber. As a plastic with an excellent gas barrier property, it is also used for packaging containers. PAN-based carbon fiber made by carbonizing acrylic filament is very strong. Toray and other Japanese companies have used it for manufacturing fishing poles, golf shafts, tennis rackets, etc. since the 1970s. Since carbon fiber is light, it has been used for aircraft parts since the late 1980s. It has also been used in the main wings and bodies of aircrafts, attracting attention since the late 2000s. Since it is also expected to be used for automotive parts and bodies, the demand for carbon fiber could expand dramatically in the future.

As a comonomer, acrylonitrile is used for manufacture of AS resin, ABS resin and synthetic rubber (NBR). Acrylonitrile is dimerized by electrolysis to give C6 adiponitrile, which is then reduced with hydrogen to give hexamethylenediamine. This process is one of the methods of manufacturing hexamethylenediamine as a raw material for 6,6-nylon.

The nitrile group of acrylonitrile is hydrolyzed to give acrylamide. A copper catalyst has been used for hydrolysis. However, in 1985, Nitto Kagaku Kogyo (now Mitsubishi Rayon) industrialized a biological method using acrylamide-producing organisms. Subsequently, biological methods using enzymes characterized by high heat resistance and good productivity have been developed. These are unique petrochemical techniques created in Japan. Acrylamide is polymerized to give polyacrylamide. Polyacrylamide is used as a flocculant for wastewater treatment, as a mud-solidifying stabilizer for drilling oil wells, and in the paper industry as a yield-improving agent, a filtering agent and a paper-strengthening agent. Since polyacrylamide as a water-soluble polymer increases the viscosity of water, it is also used as a thickener for enhanced oil recovery (EOR) [Footnote 17].

Compounds with reactive hydrogen such as amine, alcohol and aldehyde are added to

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[Footnote 17] A method of increasing the production of crude oil by injecting water and gas into oil wells that are running dry.

the double bond of acrylonitrile to cause cyanoethylation. Amine is obtained by the reduction of cyanoethyl compounds with hydrogen, while carboxylic acid is obtained by the hydrolysis of these compounds. These processes are important reactions for producing cationic surfactants and amphoteric surfactants. As mentioned above, acrylonitrile is used not only as a monomer but also as an organic intermediate.

(8) Acrolein, acrylic acid and acrylic acid esters

There have been several methods used for manufacturing acrylic acid. However, at present, acrylic acid is mainly produced by oxidizing the methyl group of propylene and then oxidizing the resulting acrolein (see Section 6.1.2 (2) 4)). This process was developed by Nippon Shokubai and Mitsubishi Chemical. Acrylic acid is reacted with various alcohols to give acrylic acid esters.

Acrylic acid undergoes radical polymerization to give polyacrylic acid as a water-soluble polymer. As polyacrylic acid catches calcium ions, etc. in water, it is used as a builder for synthetic detergents. However, in Japan, zeolite is used exclusively as a builder, while polyacrylic acid is rarely used for this purpose. When acrylic acid and acrylic acid sodium are copolymerized in the presence of a polyhydric alcohol ester of acrylic acid as a crosslinking agent, superabsorbent resin is obtained. While starch-based superabsorbent resins, etc. are also available, acrylic acid-based is the most widely used. Copolymers of acrylic acid esters with metacrylic acid esters, vinyl acetate, etc. are used as acrylic coatings. A great variety of coatings such as aqueous, thermoplastic and ultraviolet curable coatings can be made by using various ester groups.

Figure 3.16 shows the uses of acrolein. The greatest use is acrylic acid. However, because acrolein is a very reactive aldehyde, it is also used as an organic intermediate for methionine as an essential amino acid (amino acid pharmaceuticals and feed additives), glutaraldehyde (sterilizing disinfectants, leather tanning agents and fiber treating agents) and 1,3-propanediol.

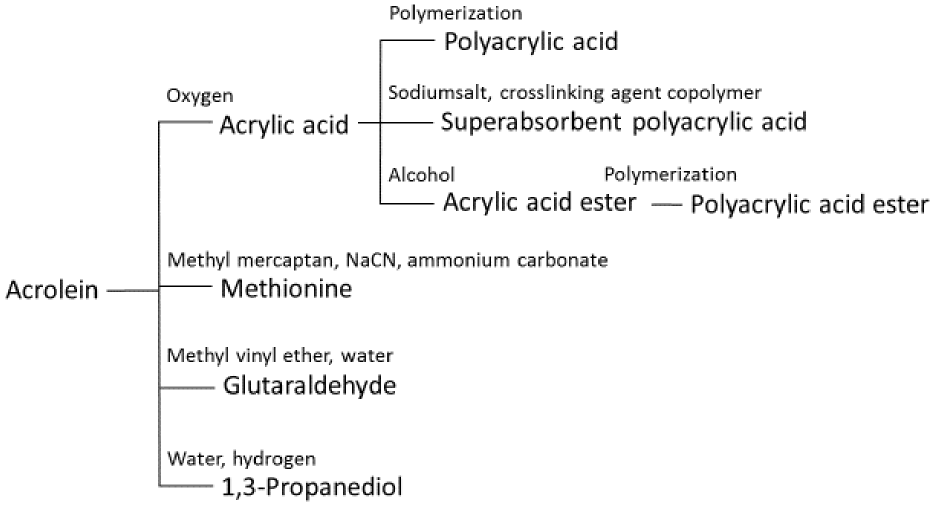

Fig. 3.16 Major product categories from acrolein.

(9) Allyl chloride and epichlorohydrin

When propylene is reacted with chlorine at 500°C, allyl chloride is produced by highly selective chlorination of the methyl group rather than an addition reaction to the double bond. A major use of allyl chloride is the manufacture of epichlorohydrin. Epichlorohydrin is obtained when chlorine water (hypochlorous acid) is allowed to act on allyl chloride and is then dehydrochlorinated with an alkali. This manufacturing process is the same as for propylene oxide. Since epichlorohydrin has two functional groups, i.e., epoxy and chlorine groups, it is used as a monomer for the production of epoxy resin. Epoxy resin is used for adhesives and semiconductor sealing materials. There has also been a growing recent demand for epoxy resin as a matrix resin (impregnation resin) for carbon fiber.

Glycerin can be synthesized from either allyl chloride or epichlorohydrin, and these processes were industrialized. However, synthesis of glycerin declined from the 2000s, because biodiesel oil began to be produced in large quantities from fats and oils such as palm oil, resulting in the production of high amounts of glycerin as a byproduct.

3.4.4 Products from the C4 and C5 fractions

C4 olefins produced by steam cracking of naphtha include butadiene and four kinds of butylene, which are separated and purified as necessary. Of these, butadiene is the most important. Figure 3.17 shows the main product categories from butadiene.

(1) Polymers from butadiene

Synthetic rubber called diene-based rubber is produced by the polymerization and copolymerization of butadiene. Styrene-butadiene rubber (SBR) obtained by the copolymerization of butadiene and styrene and butadiene rubber (BR) obtained by polymerization of butadiene alone are termed as general purpose rubber. The consumption of general purpose rubber is high, being comparable to that of natural rubber and isoprene rubber (IR), mentioned below. Both SBR and BR are used in large quantities for tires and are also widely used for rubber shoes, industrial parts, rubber-coated cloth, paper coatings, etc. BR is used for golf ball cores and high impact polystyrene (HIPS).

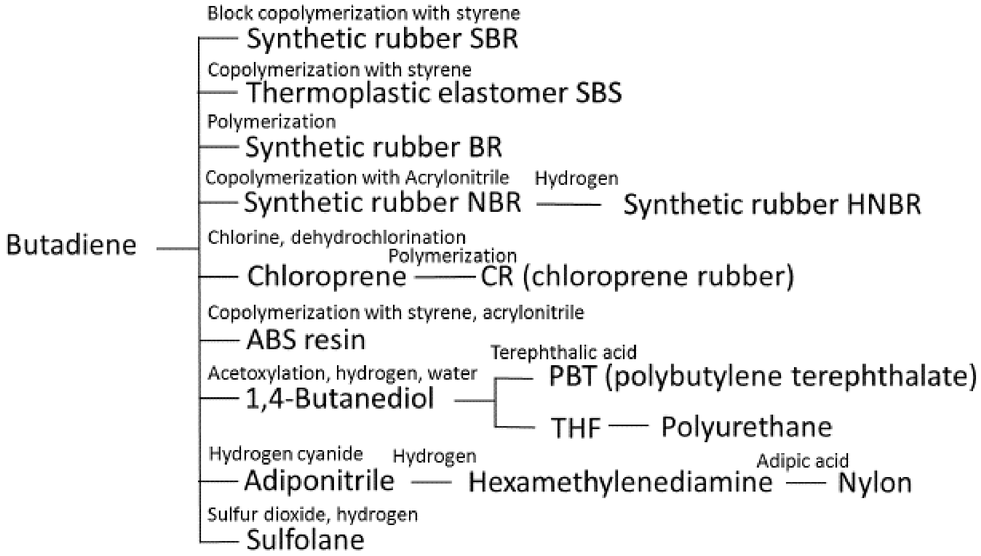

Fig. 3.17 Major product categories from butadiene.

Nitrile rubber (NBR) is formed by the copolymerization of butadiene and acrylonitrile. Hydrogenated nitrile rubber (HNBR), in which the double bond of NBR is hydrogenated almost completely, is improved with respect to weather resistance. Both NBR and HNBR are special rubbers that have outstanding oil resistance. These are used for oil-resistant hoses, tank lining and packing. Chloroprene is obtained by reaction with chlorine and butadiene. Chloroprene is polymerized to give chloroprene rubber (CR). CR is used for belts, hoses, adhesives, wire coating, etc.

The reaction used for the manufacture of synthetic rubber from conjugated diene is 1,4 polymerization [Footnote 18], which makes use of the characteristics of conjugated double bonds. As a result of this reaction, the double bonds at positions 1 and 3 of

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[Footnote 18] When the double bond of conjugated diene ($CH_2=CH-CHR=CH_2$) is polymerized alone by addition reaction to make the polymerization chain $-CH_2-CH(CHR=CH_2)-$, the reaction is called 1,2 polymerization, while when the two double bonds are allowed to act concertedly to make the polymerization chain $-CH_2-CH=CHR-CH_2-$, the reaction is called 1,4 polymerization. The double bond is left on the side chain in 1,2 polymerization, while it is left on the main chain in 1,4 polymerization. The binding direction of the main chain around the double bond (cis or trans) may be in disorder or regulated.

conjugated diene move to position 2 and remain there. In the vulcanization of rubber, this double bond is partially reacted with sulfur to make the rubber elastic. For polymerization and copolymerization from conjugated diene, radical polymerization and ionic polymerization are used depending on the expected product. Radical polymerization is further classified into radical polymerization, using an ordinary polymerization initiator, and redox polymerization, in the presence of a redox system at low temperature. In ionic polymerization, alkali metals, organic metals, the Ziegler-Natta catalyst, etc. are used on a case-by-case basis. Polymerization is performed as emulsion polymerization or solution polymerization depending on the type of rubber. Polymerized products are also classified as solid products that are coagulated so as to be used as raw materials for rubber-molded products, and latex, which is left emulsified.

Thermoplastic elastomers SBS (styrene-butadiene-styrene block copolymer) are obtained by the block copolymerization of butadiene and styrene. SBS is a block copolymer that is composed of a polystyrene portion as a hard segment and a BR portion as a soft segment. ABS resin is obtained by the copolymerization of butadiene, styrene and acrylonitrile.

(2) Industrial organic chemicals from butadiene

Butadiene that is used as a raw material of polymers is also used for the manufacture of industrial organic chemicals. 1,4-Diacetoxy-2-butene is obtained by 1,4-addition of acetic acid to butadiene. 1,4-Diacetoxy-2-butene is reduced with hydrogen and then hydrolyzed to give 1,4-butanediol and acetic acid. The acetic acid is reutilized. 1,4-Butanediol is copolymerized with terephthalic acid to give polybutylene terephthalate (PBT), a general purpose engineering plastic. Tetrahydrofuran (THF) is produced from 1,4-butanediol by dehydration. THF is used as a solvent and undergoes ring-opening polymerization to give polytetramethylene glycol (PTMG). PTMG is copolymerized with MDI to give polyurethane elastic fiber.

When hydrogen cyanide is added in 2 steps to the double bond of butadiene, adiponitrile that is a C6 industrial organic chemical is obtained (see Section 3.4.1 (5)).

Sulfolene is obtained by 1,4-addition of sulfur dioxide to butadiene, while sulfolane is obtained by the hydrogenation of sulfolene. Sulfolane is used as a solvent for extractive distillation and gas purification.

(3) Industrial organic chemicals and polymers from isobutylene

Isobutylene is the next most important C4 basic chemical to butadiene. Figure 3.18 shows the product categories made from isobutylene.

Isobutylene is readily reacted with water to give tert-butyl alcohol in the presence of an acid catalyst. As mentioned above, this reaction is also used for separating isobutylene (see Section 3.3.3 (2)). tert-Butyl alcohol is dehydrated to give isobutylene.

Methyl methacrylate (MMA) is made from isobutylene or tert-butyl alcohol as a starting material. This process is similar to the reaction for producing acrolein and then acrylic acid by oxidizing the side-chain methyl group while retaining the double bond of propylene.

Isobutylene is copolymerized with small quantities of isoprene to give butyl rubber (isobutylene isoprene rubber [IIR]). Butyl rubber has specific physical properties, because most of the bonds in the main chain are saturated. It is outstanding in aging resistance and ozone resistance and is characterized by very low gas permeability. Due to these merits, it is used for tire tubes, inliners for tires, roofing, etc.

Isobutylene is directly reacted with methanol to give methyl tert-butyl ether (MTBE). MTBE was used as gasoline additives, but its use was later prohibited. This course of events is outlined in Section 5.5.2 (3) 3).

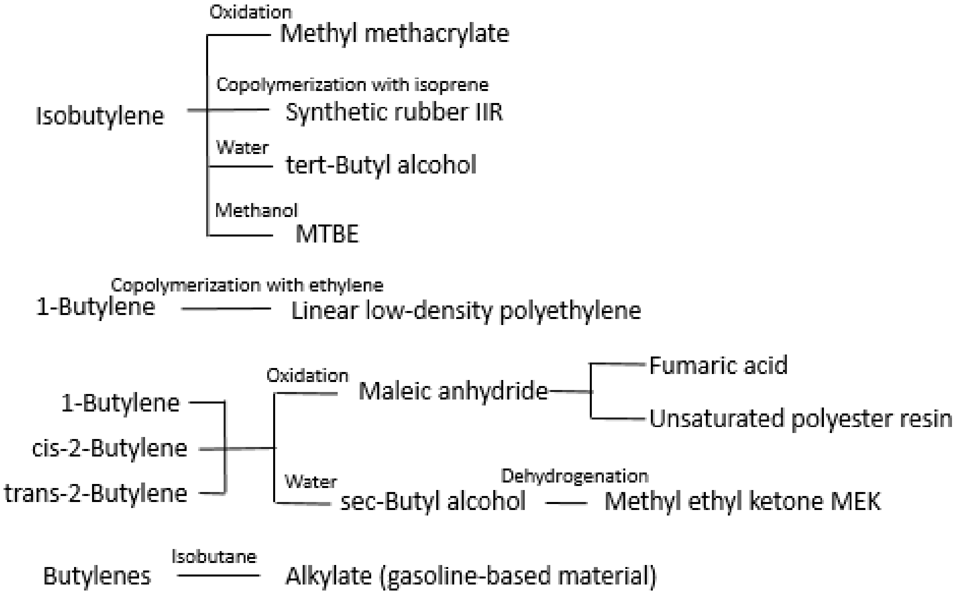

Fig. 3.18 Major product categories from butylenes.

(4) Industrial organic chemicals and polymers from n-butylene

Figure 3.18 shows the industrial organic chemicals and polymers made from n-butylene (normal butylene) (a mixture of 1-butylene, cis-2-butylene and trans-2-butylene). n-Butylene was often used without separation for the production of industrial organic chemicals. However, the importance of 1-butylene has increased rapidly since the use of L-LDPE spread worldwide in the 1980s, and it has since been separated and purified.

n-Butylene is oxidized with air to give maleic anhydride. However, since the method of manufacturing maleic anhydride by oxidation with n-butane was developed, production of maleic anhydride via n-butylene has decreased in significance. When water is added to n-butylene as a mixture in the presence of an acid catalyst, sec-butyl alcohol is obtained. sec-Butyl alcohol is oxidized to give methyl ethyl ketone (MEK), which is widely used as a solvent.

Butylenes that are not separated or purified are reacted with isobutane in the presence of a fluoric acid catalyst to give C8 branched paraffins. Petroleum waste gas containing propylene and butylene is sometimes used as it is for reaction with isobutane to give C7 to C8 branched paraffins. These branched paraffins, also called alkylates, are gasoline-based materials (see Section 2.1.2 (5)).

(5) Main industrial organic chemicals and polymers from the C5 fraction

Figure 3.19 shows the product categories produced from the C5 fraction. Important basic petrochemicals that are separated and purified from the C5 fraction include cyclopentadiene and isoprene (see Section 3.3.3 (2)). The methods of separating these chemicals have already been mentioned. The resulting residue after separating these substances and the C5 fraction is polymerized to give petroleum resin, a cheap polymer that is used for coatings for white street markings and adhesives.

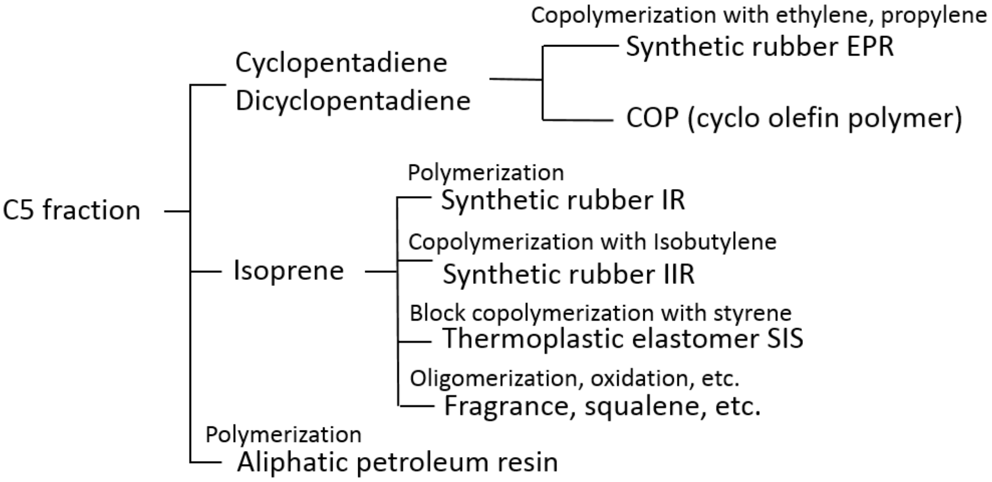

Fig. 3.19 Major product categories from products with C5.

Dicycylopentadiene is the important third component for producing EPR by copolymerization with ethylene and propylene (see Section 3.4.3 (2)). When heated, dicyclopentadiene is cracked to give cyclopentadiene. Cyclopentadiene or dicyclopentadiene undergoes ring-opening metathesis polymerization or copolymerization with ethylene followed by reduction to give various kinds of COP (cycloolefin polymers) and copolymers. COP is used as an optical material, because it is noncrystalline, very transparent, and not hygroscopic.

A significant use of isoprene is the manufacture of synthetic rubber (isoprene rubber, IR). Isoprene undergoes stereospecific polymerization in the presence of a Ziegler-Natta catalyst to give cis-1,4-polyisoprene. The structure of this polymer is the same as that of natural rubber. Isoprene is added in small quantities for copolymerization with isobutylene to give synthetic rubber (isobutylene isoprene rubber, IIR). Due to the addition of isoprene, IIR is a sulfur-vulcanizable rubber. A block copolymer with a polystyrene-polyisoprene-polystyrene structure like SBS is obtained. It is a thermoplastic elastomer called styrene-isoprene-styrene block copolymer (SIS). In addition, many synthetic perfumes are produced by the dimerization of isoprene followed by oxidation. Raw materials for cosmetics such as squalane, pharmaceutical products and intermediates for pesticides are made from oligomers of isoprene.

3.4.5 Products from the C6 fraction

The main C6 basic petrochemical is not an olefin but benzene, an aromatic hydrocarbon. Figure 3.20 shows the main industrial organic chemicals and polymers made from benzene. In the same way that an addition reaction is the core reaction in olefins, a substitution reaction plays the most important role in benzene reactions. In Fig. 3.20, all the reactions of benzene except hydrogenation to give cyclohexane are substitution reactions.

(1) Ethylbenzene, cumene and linear alkylbenzene

The formation of ethylbenzene by the reaction with ethylene and benzene and the formation of styrene by dehydrogenation have already been mentioned in the “Ethylene” section (see Section 3.4.2 (3)).

The formation of cumene by the reaction with propylene and benzene and the formation of phenol and acetone by oxidizing cumene to a peroxide and then cleaving it with an acid have already been mentioned in the “Propylene” section (see Section 3.4.3 (3)) Since phenol is an important industrial organic chemical, it is described in another section.

Linear alkylbenzene is also made from α-olefin and benzene. The hydrogen in the aromatic ring of linear alkylbenzene is replaced by a sulfonic acid group using sulfuric acid anhydride to give linear alkylbenzene sulfonate. Linear alkylbenzene sulfonate is an important anionic surfactant, which is used in large quantities for synthetic detergents.

(2) Phenol

As shown in Fig. 3.21, many industrial organic chemicals and polymers are made from phenol.

Phenol undergoes addition condensation with formaldehyde to give phenol resin (see Section 6.1.3 (2)).

Bisphenol A is obtained from acetone and phenol by reaction similar to the reaction of formaldehyde and phenol. As bisphenol A is an industrial organic chemical with 2 hydroxy groups (-OH) of phenol, it is widely used as a monomer. It is polymerized with phosgene and epichlorohydrin to give polycarbonate and epoxy resin, respectively. Polycarbonate is a polymer with superior transparency, impact resistance and flame resistance. It is widely used in consumer electrical appliances, automobiles, building materials, etc. A common example is its in the transparent substrates of CDs and DVDs. The production of polycarbonate has increased since the 1990s and it has grown into a large-scale product. Epoxy resin has already been mentioned in the “Epichlorohydrin” section (see Section 3.4.3 (9)). Other small-scale polymers such as polysulfone and polyetherimide are obtained from bisphenol A. Polysulfone is often used for filters in artificial kidneys. Polyetherimide is a super engineering plastic in which improves the molding processability of polyimide.

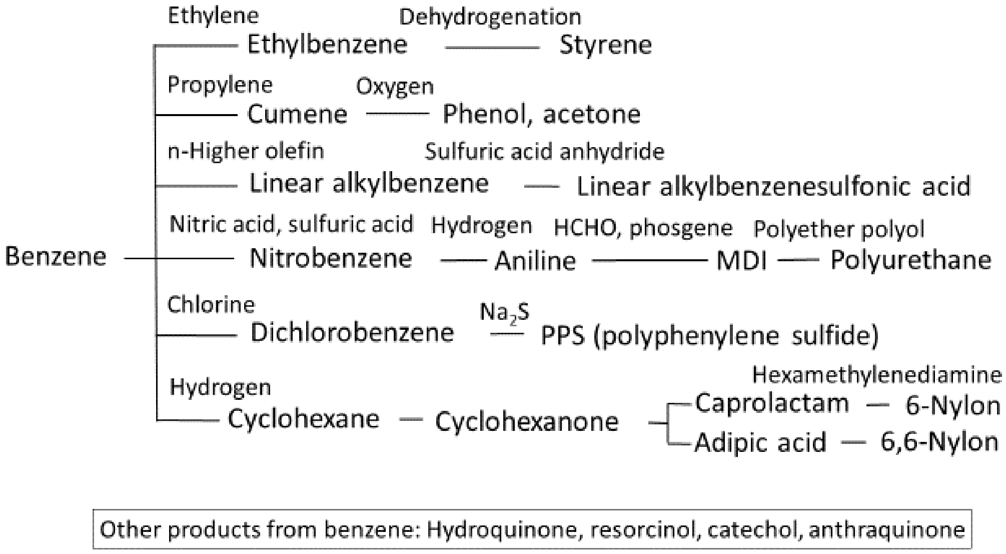

Fig. 3.20 Major product categories from benzene.

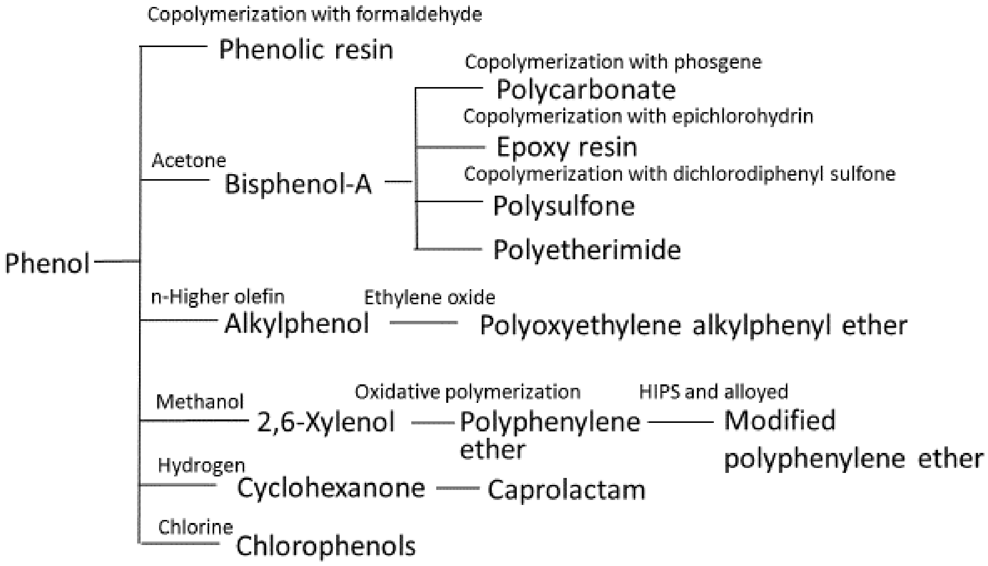

Fig. 3.21 Major product categories from phenol.

Similar to the reaction between benzene and ethylene or propylene mentioned in the preceding section, alkylphenol is obtained by a reaction between α-olefin and phenol. Ethylene oxide is reacted with the hydroxy group of alkylphenol to give polyoxyethylene alkylphenyl ether. It is used as a nonionic surfactant.

The hydrogen atoms at positions 2 and 6 of phenol are replaced by methyl groups using methanol to give 2,6-xyrenol. When 2,6-xyrenol undergoes oxidative polymerization (oxidative coupling) in the presence of a copper catalyst, only the para position (position 4) of phenol reacts, giving polyphenylene ether in which aromatic rings and oxygen are connected linearly. The processability of polyphenylene ether is poor. However, because it mixes well with polystyrene to give a marked improvement in processability, it is usually used as a mixture with such a polymer (called a polymer alloy). Polyphenylene ether is also known as modified polyphenylene ether (PPE).

Phenol is reacted with chlorine to replace some of the hydrogen atoms in the aromatic ring with chlorine groups to give chlorophenol. Chlorophenol is used as an intermediate for pesticides.

The method of manufacturing caprolactam by hydrogenation of phenol via cyclohexanone is an old process. However, it is often used even now and is an important use of phenol in the United States and Europe. The method of manufacturing caprolactam by hydrogenation of benzene is described later in the “Cyclohexane” section.

(3) Nitrobenzene and aniline

Benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid to give nitrobenzene (Fig. 3.20). Nitrobenzene is reduced with hydrogen to give aniline. Aniline is an important organic intermediate for synthetic dyes, and is also used in large quantities as a raw material for MDI (4,4’-diphenylmethane diisocyanate) in the petrochemical industry. Aniline is reacted with formaldehyde in the presence of an alkali to give 4,4’-diaminodiphenyl methane. This reaction is similar to the reaction to obtain bisphenol A from phenol and acetone, mentioned previously. Hydrogen at the para position of the aromatic ring is replaced by a methylene group derived from aldehyde, and aniline is connected. When 4,4’-diaminodiphenyl methane is reacted with phosgene, the amino group changes to an isocyanate group to give MDI. MDI is reacted with polyether polyol to give polyurethane.

(4) Chlorobenzene

Benzene is reacted with chlorine to give chlorobenzene, in which some of the hydrogen atoms in the aromatic ring are replaced by chlorine (Fig. 3.20). Monochlorobenzene is reacted with trichloroacetaldehyde to produce an insecticide (didchlorodiphenyl-trichloroethane [DDT]). DDT used to be a significant chemical in terms of public health and agriculture, although its production is now prohibited. Monochlorobenzene is mainly used as a solvent, for instance, in the reaction of 4,4’-diaminodiphenyl methane and phosgene, mentioned in the preceding section.

Paradichlorobenzene is used for insecticides and deodorants. It is polymerized with sodium sulfide to give polyphenylene sulfide (PPS). Due to its outstanding heat resistance and mechanical strength, PPS is used as an engineering plastic.

(5) Cyclohexane, adipic acid and caprolactam

The reaction in which the aromatic ring of benzene is destroyed by hydrogenation to give cyclohexane is very unique, because benzene usually undergoes substitution reactions. Cyclohexane is also contained in catalytic reformates and cracked gasoline. However, due to the difficulty in separation and purification, it is exclusively produced by the hydrogenation of benzene. It is used as a solvent, and also oxidized to give cyclohexanone and cyclohexanol, and subsequently adipic acid and caprolactam (see Section 6.1.2 (4)). Adipic acid is reacted with hexamethylenediamine by condensation polymerization to give 6,6-nylon. Caprolactam undergoes ring-opening polymerization to give 6-nylon. Nylon (polyamide) is used for synthetic fibers and engineering plastics.

3.4.6 Products from the C7 and C8 fractions

Like main C6 basic petrochemicals, main C7 and C8 basic petrochemicals are not olefins, but rather aromatic hydrocarbons, namely toluene and xylene. Ethylbenzene, a C8 aromatic hydrocarbon, is also obtained from cracked gasoline. However, because it is usually synthesized from ethylene and benzene, it has already been described as an ethylene product. Figure 3.22 shows the main product categories made from toluene and xylene.

(1) Industrial organic chemicals from toluene

As a solvent, toluene is often used for coatings, adhesives, etc. TDI, shown in Fig. 3.22, is one of the main industrial organic chemicals obtained from toluene. In the same way that aniline is made from benzene, toluene is initially nitrated with concentrated nitric acid and concentrated sulfuric acid to give dinitrotoluene. This process is a substitution reaction in which the hydrogen in the aromatic ring is substituted by nitro groups. The dinitrotoluene is then reduced with hydrogen to give diaminotoluene, which is then reacted with phosgene to give TDI.

TDI, as well as MDI, is a diisocyanate that is produced in large quantities. TDI is reacted with polyether polyol to give polyurethane. Polyurethane is mainly used in the manufacture of flexible polyurethane foam and is also used for polyurethane coatings, polyurethane adhesives and polyurethane rubber.

However, apart from TDI, there are no large-scale industrial organic chemicals produced from toluene. Consequently, , the demand for toluene in the petrochemical industry is small in proportion to the amount of toluene produced alongside benzene and xylene when extracting aromatic hydrocarbons from cracked gasoline and catalytic reformates, resulting in excessive amounts of toluene being produced. At petrochemical plants, this excessive toluene is made into benzene and xylene by a disproportionation reaction.

(2) Industrial organic chemicals from xylene

Xylene has three types of isomer (ortho, metha and para). The main industrial organic chemical produced from xylene is carboxylic acid obtained by the oxidation of both methyl groups (see Section 6.1.2 (3) 1)). This reaction is not a substitution reaction, as is characteristic of aromatic hydrocarbons, but is similar to the reaction in which the methyl group of propylene is oxidized to give acrylic acid. However, because the mechanism of reaction is quite different, these reactions are only similar in style.

Phthalic anhydride is made from o-xylene by oxidation. Phthalic anhydride is reacted with 2-ethylhexanol to give a plasticizer (DOP). The plasticizer is used together with polyvinyl chloride to produce flexible polyvinyl chloride products (films, hoses, leather, wire coating, etc.). Phthalic anhydride is also reacted with various alcohols such as isodecyl alcohol and used as a raw material for various phthalate ester-based plasticizers. It is also reacted with polyhydric alcohol and maleic anhydride by condensation polymerization to give unsaturated polyester resin. As a glass fiber-reinforced plastic, unsaturated polyester resin is used for the manufacture of large molded articles such as fishing boats, tanks and bathtubs. It has also long been used as a raw material for alkyd resin.

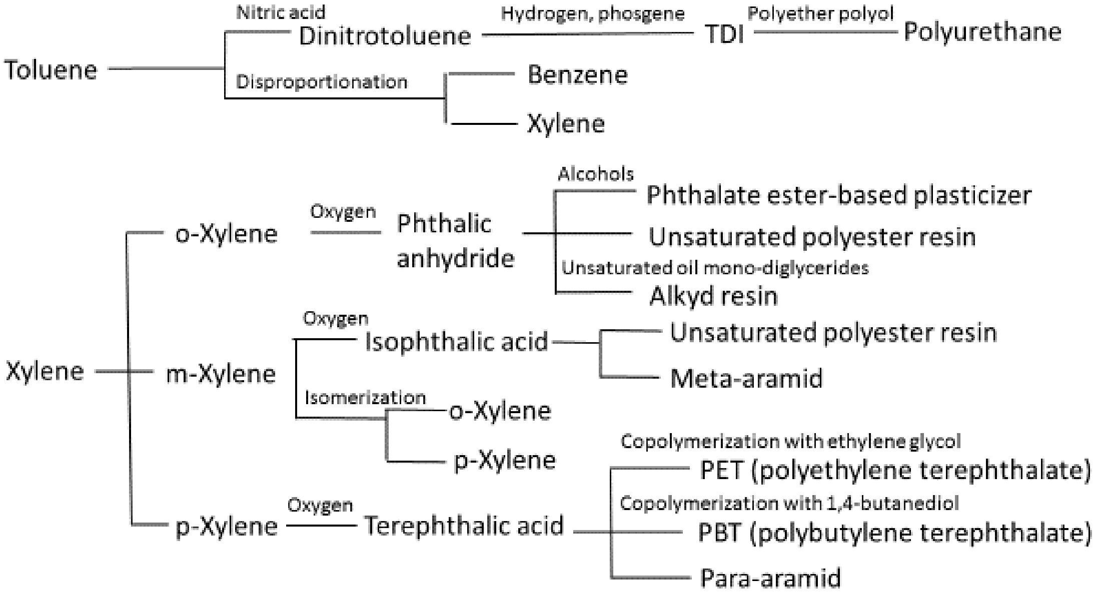

Fig. 3.22 Major product categories from toluene, xylene.

m-Xylene is oxidized to give isophthalic acid. Isophthalic acid is used for unsaturated polyester resin. However, unlike phthalic anhydride, it is not used as a main monomer, only for reforming. When isophthalic acid changes into a highly reactive acid chloride, then reacted with m-phenylenediamine by condensation polymerization, it gives meta-aramid (wholly aromatic polyamide). Since meta-aramid has outstanding heat resistance and flame resistance, it is used for space suits, firefighting uniforms, curtains, etc., albeit in small quantities.

p-Xylene is oxidized to give terephthalic acid. Terephthalic acid is reacted with EG by condensation polymerization to give PET. Polyester fiber has dominated nylon and acrylic fibers and is currently considered to be the most important synthetic fiber. In the form of PET resin, terephthalic acid is used in large quantities for bottles, films, tapes, etc. It is also reacted with 1,4-butanediol by condensation polymerization to give PBT. PBT is widely used as an engineering plastic. Terephthalic acid is changed to acid chloride and is then reacted with paraphenylenediamine by condensation polymerization to give para-aramid. As a very strong fiber, para-aramid is used for tire cords, bulletproof vests, safety globes, etc. As mentioned above, terephthalic acid is a large-scale industrial organic chemical having a much greater demand than not only isophthalic acid but also phthalic anhydride.

Compared with o-xylene and p-xylene, m-xylene has a much smaller demand. Meanwhile, the isomer ratio of xylene obtained from catalytic reformates and cracked gasoline is almost constant. Therefore, surplus m-xylene has been isomerized in the presence of an acid catalyst to give a mixture of o-, m- and p-xylene and then o- and p-xylene have been separated and purified (see Section 6.1.1 (6)).

3.4.7 Products from the ten or more fractions

Industrial organic chemicals from the ten or more carbon atoms include many important surfactants. The greatest use of surfactants is synthetic detergents. To prevent environmental contamination with foam, synthetic detergents must be promptly degraded by microorganisms after discharge into the environment. To achieve this, the carbon chains must be straight. However, basic petrochemical products with more than C10 that can be used as raw materials of ssurfactants cannot be produced by steam cracking of naphtha. As shown in Fig. 3.23, there are three starting materials.

One of the three routes is the extraction of linear n-paraffin from kerosene as a petroleum fraction having more carbon atoms than naphtha (Fig. 3.23 [1]). n-Olefin is obtained by the thermal cracking of n-paraffin. The molecule of n-olefin is a straight carbon chain with a double bond at the end or inside. The second route is the production of α-olefin from ethylene as a starting material (Fig. 3.23 [2]), as mentioned in Section 3.4.2 (7). In the third route, fats and oils are used as raw materials rather than petroleum or natural gas (Fig. 3.23 [3]). For this reason, this route is considered to conflict with the definition of petrochemistry. Nevertheless, petrochemical techniques can be applied to the manufacture for surfactants from the raw materials of fats and oils. Fats and oils are higher fatty acid triglycerides. Triglycerides composing fats and oils are mostly C12 to C18 linear carboxylic acids.

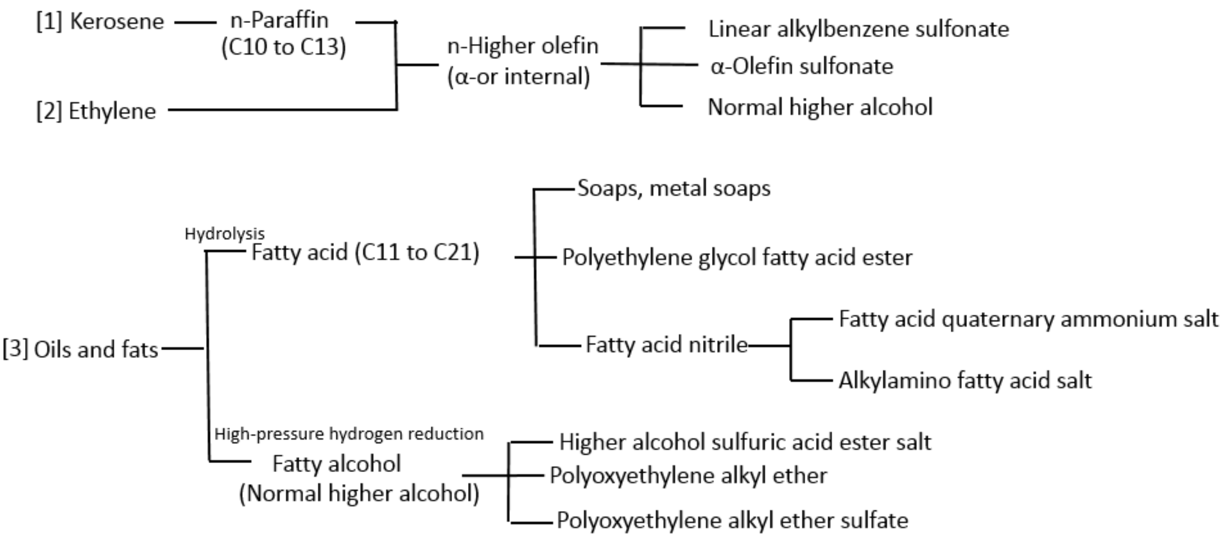

Fig. 3.23 System of product from C10.

(1) Industrial organic chemicals from olefins with ten or more carbon atoms

Linear alkylbenzene is obtained by a reaction between the n-olefins (including α-olefin) shown in Fig. 3.23 [1], [2] and benzene. Sulfonic acid is then introduced into the aromatic ring using sulfuric acid anhydride and neutralized with an alkali to give linear alkylbenzene sulfonate. Linear alkylbenzene sulfonate is a linear anionic surfactant (linear alkylbenzene sulfonate [LAS]) with outstanding cleaning properties. It is used in large quantities for detergents.

When α-olefin is sulfonated by reaction with sulfuric acid anhydride and then hydrolyzed, the double bond shifts internally during the reaction. This results in α-olefin sulfonic acid being obtained, although the position of the double bond is different in this mixture. It is neutralized with an alkali to give α-olefin sulfonate. This is used as an anionic surfactant (α-Olefin sulfonate [AOS]) with outstanding biodegradability.

After the oligomerization of ethylene, linear higher alcohols are obtained by oxidation and hydrolysis. Linear higher alcohols having one more carbon atom than the original olefin can also be obtained by the oxo process of α-olefin. The uses of linear higher alcohols are described in the next section.

(2) Industrial organic chemicals from fats and oils

Higher fatty acid (C12–C18) obtained by the high-pressure hydrolysis of fats and oils (Fig. 3.23 [3]) is neutralized with an alkali to give soap and metallic soap. Soap that is a sodium salt of higher fatty acids has long been produced as a detergent and also as an anionic surfactant. Calcium salt, magnesium salt, barium salt, zinc salt, etc. of higher fatty acids are termed as metallic soap. Metallic soap is used for plastic stabilizers and lubricants/mold release agents.

Higher fatty acids react with ethylene oxide to give a polyethylene glycol fatty acid ester that is used for nonionic surfactants. Higher fatty acids also react with ammonium to give amide, which is then dehydrated to give fatty acid nitrile. Fatty acid nitrile is reduced to give primary to tertiary fatty amine, which is then reacted with methyl chloride to give a quaternary fatty acid ammonium salt. This substance is used as a cationic surfactant. Acrylonitrile is added to primary fatty acid amine (cyanoethylation) and then the nitrile group is hydrolyzed and neutralized to give an alkylamino fatty acid salt. Since this substance has both amino and carboxy groups within the molecule and also has a long-chain alkyl group, it is used as an amphoteric surfactant.

Higher fatty acid of fats and oils are also reduced by high-pressure hydrogene to give fatty alcohol (linear higher alcohol). In fact, to accelerate the reaction, fats and oils are subjected to ester exchange with methanol to give a higher fatty acid methyl ester, which is then hydrocracked. Higher alcohol is esterified with chlorosulfuric acid or anhydrous sulfuric acid and then neutralized with an alkali to give a higher alcohol sulfuric acid ester salt. This is an anionic surfactant (alkyl sulfuric acid ester salt [AS]) used as a neutral detergent with stable quality. Higher alcohol is polymerized with ethylene oxide to give polyoxyethylene alkyl ether. This is a nonionic surfactant (AE). It is further changed into a sulfate ester salt to give polyoxyethylene alkyl ether sulfate. This is an anionic surfactant polyoxyethylene alkyl sulfate (AES). Higher alcohol is reacted with dimethylamine to give tertiary aliphatic amine.

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4 Industrial organic chemicals and polymers predating petrochemistry

Even before the establishment of the petrochemical industry, there had been fully-fledged industrial organic chemical industries and polymer industries based on wood, carbohydrates (fermentation), fats and oils and coal since the late 19th century. Of course, industrial organic chemicals and polymers were being produced before that, such as highly-concentrated ethanol from alcohol distillation, vinegar (acetic acid aqueous solution) from acetic acid fermentation of alcohol, soap made by boiling fats and oils with alkalis, coatings from unsaturated oils and lacquers and adhesives from glue or starch paste. However, these were by no means modern chemic al industries. Accordingly, this chapter discusses the industrial organic chemical and polymer industries that existed from the late 19th century onwards.

These industrial organic chemical and polymer industries developed in significantly different ways in various different regions, depending on the availability of raw materials and the different product demands. These industries were individually taking shape in the forest of petrochemstry, as mentioned in the previous chapter. As shall be mentioned later, two forests sprang up from wood, and three from coal. In terms of technology, Germany, the United States and the United Kingdom were the developed nations. However, even Japan developed fully-fledged industrial organic chemical and polymer industries from the 1930s onwards, using various different raw materials. This laid the foundation for Japan’s quick uptake and rapid development of petrochemical technology from the late 1950s onwards.

Petrochemistry originated in the United States in the 1920s, and existed alongside other pre-existing industrial organic chemical and polymer industries in the United States up until the 1940s. The forest of petrochemistry stayed small for the first three decades of its existence in its native habitat, the United States. There were many other forests that thrived more than the forest of petrochemistry. However, that forest grew rapidly within a short space of time in the 1950s and the 1960s, in the United States, in Europe and also in Japan. It either absorbed or overshadowed the pre-existing forests of industry that had developed alongside it. Accordingly, many of the petrochemical products discussed in the previous chapter were developed in industries predating petrochemistry. This chapter discusses the rise and decline of these chemical industries that predated petrochemistry, citing examples from Japan.

4.1 Industrial organic chemicals and polymers from wood

There are two broad forests of chemistry using wood as a raw material, as shown in Fig. 4.1. One is industrial organic chemicals made from byproducts produced during wood carbonization, practiced since before the modern chemical industry began. The other is the use of cellulose, a natural polymer that is the main component in wood.

Industrial organic chemical industries using wood carbonization came to an end in the 1930s due to the rise of the carbide and acetylene industries, as shall be mentioned later. This took place at almost exactly the same time in Japan, the United States and Europe. Prior to the Second World War, the cellulose industries in Japan started producing a few chemical products that reached world-class production volumes (celluloid, rayon). In the late 1950s, as the petrochemistry became industrialized, the cellulose industry forest dwindled into decline as it came under pressure from the petrochemistry forest. However, some cellulose products have still survived to this day, namely fine chemical products and functional products.

4.1.1 The wood carbonization industry

When wood is carbonized to produce

charcoal, wood tar, pyroligneous acid and wood gas are produced as byproducts. Pyroligneous acid produces acetate of lime and crude methanol. Acetate of lime produces acetic acid and its salts and esters, as well as producing acetone if dry distilled. Crude methanol produces refined methanol, which in turn produces formalin.

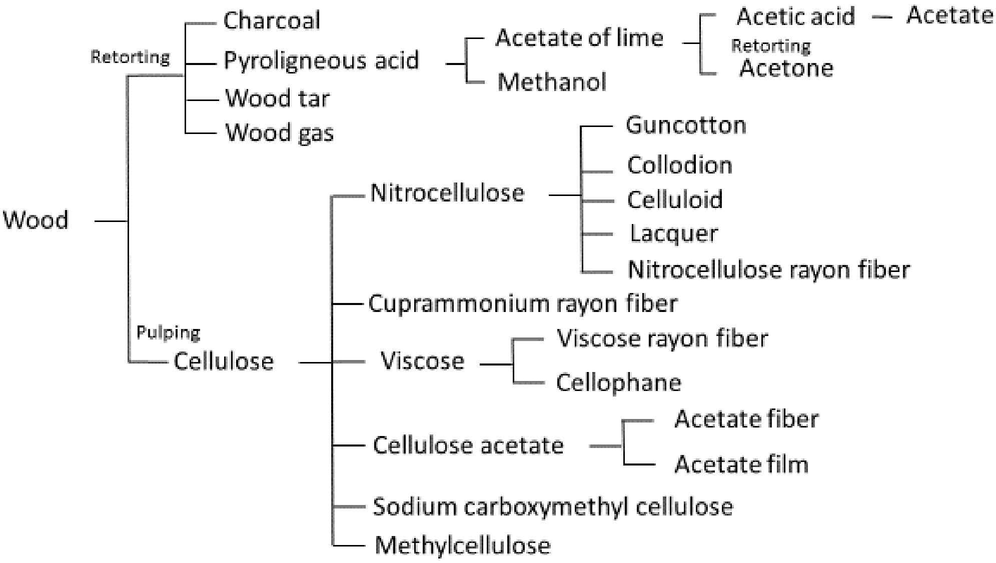
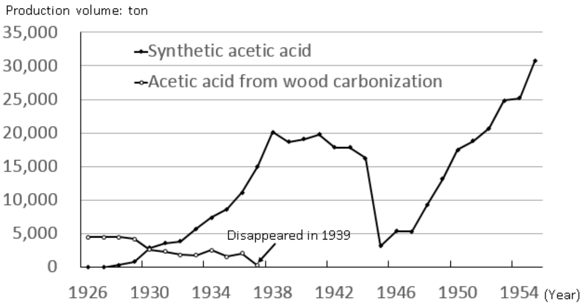


Fig. 4.1 Major product categories of wood as raw material.

Wood carbonization has been carried out since the 18th century in forest-resource-rich countries and regions such as Austria, Hungary, Northern Europe and the United States, while Germany and the United Kingdom developed acetic acid refining industries, importing acetate of lime and using it to produce acetic acid.

The wood carbonization industry in Japan began in 1893 with the establishment of a wood carbonization plant in Tochigi by Shōichirō Katō, the wealthy founder of Kato Chemicals in Nikko. Later, the demand for acetic acid for dyeing grew, and the wood carbonization industry developed, with an increasing number of small-scale manufacturers affiliated to charcoal-making facilities. However, such small-scale production could not meet the increasing demand for acetic acid. In 1902, Shōichirō Katō established The Nippon Acetic Acid Manufacturing Company (capital ¥100,000) in Honjo, Tokyo. This took over Kato Chemicals and relocated its facilities to begin large-scale acetic acid production, using mainly imported acetate of lime. This move was endorsed by the major players in the business world at the time, including Magoshi Kyōhei, Shibusawa Eiichi, Ōkura Kihachirō and Ōkawa Heizaburō. In 1907, The Nippon Acetic Acid Manufacturing Company increased its capital to ¥300,000. The company newly imported acetic acid manufacturing equipment (steam-heated, diminished-pressure crude acetic acid manufacturing equipment, acetic acid concentrated distillation apparatus, acetic acid rectification equipment) from the German company Mayer. A new plant was completed in 1908, and production of glacial acetic acid (100% acetic acid) commenced. To be more self-sufficient in raw materials, The Nippon Acetic Acid Manufacturing Company increased its capital to ¥600,000 and established a new plant in Shiobara, Tochigi, importing a suite of transportable wood carbonization equipment from Mayer for the new plant. This ushered in a new era of modern wood carbonization plants, well beyond the reach of small-scale charcoal byproduct processing. The wood was carbonized in a transportable retort or furnace (wood processing capacity of 1,000 cubic *shaku* or 27.83 m^3) and pyroligneous acid was produced by removing the wood tar from the volatile component. The pyroligneous acid was then neutralized with milk of lime in a neutralization tank. The neutralized solution was heated to evaporate the methanol, then distilled to produce crude methanol. The residual liquid from the evaporation was concentrated in a double-effect evaporator to produce a concentrated lime acetate solution. This was then dried in a cylindrical dehydrator. Annual production of 80% acetate of lime was 900 tons; annual production of 80% crude methanol was 250 tons; these products were then sent to the Honjo plant in Tokyo for refining.

Later, a number of manufacturers started entering the wood carbonization industry as the First World War disrupted the import of acetate of lime, and the market soared. Incidentally, during the war, Germany industrialized synthetic acetic acid made from carbide and acetylene, which was imported by many countries, including Japan, after the war. This was followed by a sudden increase in acetate of lime imports from the American wood carbonization industry, sending a succession of Japanese wood carbonization manufacturers into bankruptcy or mergers. In 1925, four surviving companies, including The Nippon Acetic Acid Manufacturing Company, formed the Dai Nippon Acetic Acid Manufacturers' Association, and tried to restrict production in order to achieve market stability. However, the appearance of synthetic acetic acid meant there was no future for the wood carbonization industry, and the association turned its attention to domestic production of synthetic acetic acid. The course of events that followed is discussed in the section on carbide and acetylene. With the domestic production of synthetic acetic acid, the wood carbonization industry rapidly declined, and completely disappeared by 1939, as shown in Fig. 4.2.



Source: Reference [1]

Fig. 4.2 Switchover from acetic acid from wood carbonization to synthetic acetic acid in the early 1930s.

4.1.2 Nitrocellulose

Another forest sourced from wood is the cellulose chemistry industry. Cellulose is a natural polymer and is the main component in wood and grasses. It has been used since ancient times in the form of hemp fiber, cotton and paper. However, cellulose does not melt or soften when heated, and also does not dissolve in solvent. Accordingly, naturally-available, short-fibered cellulose materials had to be utilized through physical manipulation such as spinning or paper-making. Chemical manipulation of cellulose began in the late 19th century, when it was discovered that it could be partially nitrated in concentrated nitric/sulfuric acid mixture to produce nitrocellulose, which could be dissolved in solvent, and had some plastic properties when mixed with camphor.

(1) Celluloid

An early cellulose product was collodion (liquid bandages) made by dissolving nitrocellulose in a mixture of ether and ethanol. This was followed by celluloid, made from nitrocellulose and camphor in the United States in the 1870s. In modern terms, camphor served as a plasticizer. While celluloid was arguably also industrialized in the United Kingdom in the 1850s, it was not until after it was industrialized in the United States that it became properly widespread. Celluloid was the first plastic. Initially used in daily necessaries and toys, it was also put to use in photographic film by Eastman Kodak in 1889, revolutionizing the photosensitive materials industry.

Japan started importing celluloid sheets in the late 1870s, not long after it was first invented. By the mid-1880s, celluloid sheet imports were in full swing; it was being processed to produce faux coral beads, combs, hairpins and collars. In the 1890s, a number of celluloid product manufacturers, inventors, and entrepreneurs started planning to produce celluloid sheets domestically. Despite repeated failures, including some explosion incidents, small-scale production of celluloid sheets was achieved. By the late 1900s, Mitsui, Mitsubishi, Suzuki Shoten, Iwai

Shoten and other large-capital enterprises had started production of celluloid sheets; Japanese celluloid sheet production rapidly increased around the time of the First World War. Eight of these celluloid manufacturers combined to form Dainippon Celluloid (now Daicel) in 1919.

After the First Sino-Japanese War, Japan annexed Taiwan and promoted camphor production there. By the early 1900s, Taiwan was leading the world in camphor supply. This gave the Japanese celluloid industry a competitive edge, and by 1937 Japan was producing the highest quantity of celluloid in the world (12,760 tons). This accounted for 45% of the world's celluloid; Japan was exporting 7,500 tons of celluloid sheets. Figure 4.3 shows the trends in celluloid production volumes in Japan. Celluloid production peaked between 1937 and 1940. By the late 1930s, nearly 70 companies were producing phenol resin, which had been domestically produced since 1915. Together, phenol resin and celluloid dominated the plastics market. As a thermoplastic, celluloid had an advantage over thermosetting phenol resin, making for a formidable rival in the market.

Source: Reference [8]

Fig. 4.3 Change of production volume of celluloid.

The celluloid industry resumed production soon after the Second World War, exporting toys and daily necessaries. By the late 1950s, however, it started to come under pressure from polyvinyl chloride in the rising acetylene industry; once the petrochemical industry started domestic production with a succession of new polymers (mostly thermoplastics such as polyethylene, polystyrene, etc.), the sun began to set on celluloid. With the successive emergence of celluloid-substitute thermoplastics, the main drawback with celluloid – its combustibility – was a major factor in its losing much of its demand in the market for toys and daily necessaries. After that, celluloid production in Japan started to wane, stopping altogether in 1996.

(2) Lacquer

A butyl acetate solution of nitrocellulose was also used in coatings. This was called nitrocellulose lacquer. Quicker to dry than existing coatings made from unsaturated fats and oils, nitrocellulose lacquer revolutionized the automotive coating industry. One well-known brand was Duco coating, produced by DuPont in 1923. Nitrocellulose lacquer is still used for coating leather, synthetic leather, wooden articles, furniture, etc., due to its luster, durability and quick drying speed.

(3) Rayon fiber from soluble nitrocellulose

Ether and ethanol solutions of nitrocellulose could also be made into fibers by extruding them through a glass tube. Frenchman Hilaire de Chardonnet started industrial production of artificial fiber (rayon fiber from soluble nitrocellulose) in 1892. Because silk had been the only long-fiber material available before that, this artificial long-fiber material was known as artificial silk. As nitrocellulose had the drawback of being highly flammable, de Chardonnet denitrated the fibers by soaking them in sodium sulfide. Swiss German chemist Matthias Schweizer had discovered in 1857 that cellulose dissolved in a cuprammonium solution. Cuprammonium rayon fibers were also produced by spinning this solution in a sulfuric acid bath. By the start of the 20th century, this fiber was proving to be fierce competition for soluble nitrocellulose rayon fiber in Europe. Soluble nitrocellulose rayon was never industrialized in Japan.

4.1.3 Viscose

The cellulose-based industries were significantly transformed by the invention of viscose. Once viscose rayon fiber was industrialized in 1904 by British company

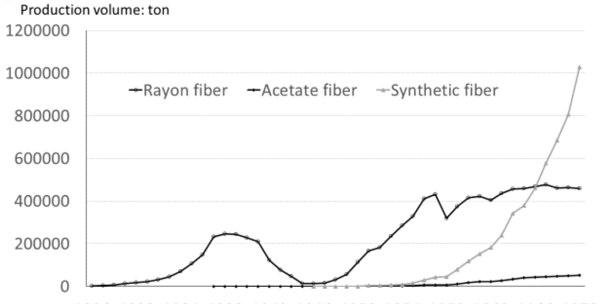
Courtaulds, this method quickly dominated rayon production in the 1910s, having lower production costs and better product quality than the soluble nitrocellulose method or the cuprammonium method. The cellulose is treated with a sodium hydroxide solution, and then has carbon disulfide added to dissolve it into sodium cellulose xanthate, in turn producing a viscous liquid (viscose). When spun in sulfuric acid, the cellulose regenerates, producing viscose rayon fiber. The viscose can also be extruded through a film-shaped slit to form cellophane.

(1) Rayon fiber

Industrialization of rayon fiber in Japan began with the viscose method rather than the soluble nitrocellulose method or the cuprammonium method. Mitsubishi, Iwai Shoten and Suzuki Shoten, mentioned in the previous section, were involved in the industry; Japan Celluloid Artificial Silk (now Daicel) was established in 1908 and its factory in Aboshi started operating in 1911. However, contrary to what the name implies, the company did not actually produce artificial silk, but solely produced celluloid sheets. Since there was fierce competition in Europe between the soluble nitrocellulose method, the cuprammonium method and the viscose method, European companies were not readily exporting technology or equipment, which meant that Japan Celluloid Artificial Silk was unable to acquire or industrialize any artificial silk technology.

Meanwhile, Itsuzō Hata of Yonezawa Higher Technical School (now Yamagata University Faculty of Engineering), with the support of Suzuki Shoten, independently developed a viscose rayon method using literature from Europe. This technology was industrialized, and the Imperial Artificial Silk Company (now Teijin) was established in Yonezawa in 1918. After the First World War, German companies started to actively supply technology, and many Japanese companies entered the viscose rayon industry using introduced technology. Short-fiber rayon was developed in 1931, and the Japanese rayon industry joined forces with the Japanese spinning industry, the strongest in the world at the time. This enabled Japan to become the world's leading rayon-producing country (245,000 tons), overtaking the United States, by 1938. This was also aided by the fact that the core of the American chemical fiber industry had shifted from viscose rayon to acetate, as shall be discussed in the following section.

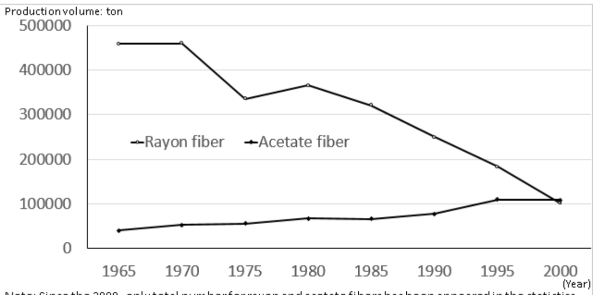
Figure 4.4 shows the trends in production volumes for rayon fiber (including cuprammonium rayon, which started being produced in small quantities in Japan from 1931), acetate fiber and synthetic fiber. The prewar peak production volume of rayon fiber was around 20 times higher than the prewar peak production volume of celluloid. This figure shows how much smaller in scale the plastics market was before the Second World War. Chemical utilization of polymer materials started with fibers rather than with plastics.



Source: Reference [5]

Fig. 4.4 Change of production volume of rayon fiber, acetate fiber and synthetic fiber.

Rayon fiber revived relatively quickly after the Second World War, topping its prewar peak in the late 1950s, as shown in Fig. 4.4, and reaching 1.8 times its prewar peak in 1957. Right at this time, full-scale production of vinylon, nylon and other synthetic fibers began. However, unlike celluloid, rayon fiber did not cede defeat to synthetic fiber, and did not fall into rapid decline. Although its growth later markedly slowed, production reached a record peak in 1967 (479,000 tons). This is thought to be because although rayon was not as strong as synthetic fiber, it was still more absorbent and also did not have any fatal flaws, such as celluloid's flammability. However, ongoing improvements were made to synthetic fibers, mainly polyester, and rayon production volumes decreased from the 1970s onwards, as shown in Fig. 4.5.



Note: Since the 2000, only total number for rayon and acetate fibers has been appeared in the statistics due to decreases in company numbers.

Source: Ministry of Economy, Trade and Industry, fiber statistics and textile and daily necessaries statistics

Fig. 4.5 Change of production volume of rayon fiber after the production peak and its being surpassed by acetate fiber.

The overall Japanese textile industry (synthetic fiber, spinning, fabric, knitting, dyeing, sewing) decreased in scale, and is presently estimated to have a production volume of only several tens of thousands of tons. By the 2000s, rayon no longer appeared in the statistics on its own, due to decreases in company numbers. Rayon is currently estimated to account for only several percent of the overall chemical fiber production volume, consisting of rayon fiber, acetate fiber and synthetic fiber combined.

(2) Cellophane

Cellophane was invented in 1908 by Swiss chemist Jacques Brandenberger. It was industrialized in 1912 by French company La Cellophane. It was industrialized in the United States in 1914 by DuPont. DuPont developed nitrocellulose-coated, moisture-proof cellophane in 1927, and demand grew significantly.

The Japanese cellophane industry started later than the rayon industry, with Kōshinsha starting production 1926. Like rayon, postwar production reached a peak around 1937, with an article in the *Manchuria Daily News* (July 21, 1938) estimating a production volume of around 6,000 tons. Cellophane production rapidly recovered after the war, topping its prewar peak in the early 1950s. Meanwhile, LDPE imports began in 1951, and production began the same year on highly productive inflation film. This cheap polyethylene film was thought to be a strong competitor against cellophane. With domestic production of LDPE starting in 1958, cellophane was expected to go into decline. However, a cellophane/polyethylene film laminate product (called Polycello) had been achieved in 1954, and by leveraging the respective strengths of both products (the flexibility and transparency of cellophane combined with the moisture resistance and heat sealing-properties of polyethylene), the two were able to develop alongside each other, mainly for packaging food products. This was an unexpected development. While it is difficult to estimate the weight of cellophane due to its being a film, cellophane industry statistics estimate that production increased by 23 times in 20 years from 1950 to 1970, reaching a volume of 100,000 tons.

However, domestic production of bi-axially oriented polypropylene (OPP) film began in 1963. OPP film could compete head on with cellophane film in terms of its transparency and flexibility. While OPP film initially made little headway due to its lack of heat sealing properties and other factors inhibiting its compatibility with packaging machines, by laminating it with cast polypropylene (CPP) or polyethylene film and with the improved heat sealing properties, the market for it rapidly grew from the late 1960s onwards. As a result, cellophane production volumes peaked in the late 1960s and rapidly declined in the 1970s. In 1974, OPP film production overtook cellophane, and the gap increasingly widened from then on. In 1980, cellophane production had dropped to around 50,000 tons, less than half that of OPP film. Although cellophane production has continued to decline, there are still applications for it, and it is still being produced. More recently, cellophane has gained some attention for its biodegradability.

4.1.4 Acetate

Acetate, which is produced by reacting cellulose with acetic anhydride, was developed during the First World War as an aircraft coating resin. British company Celanese started industrial production of acetate fiber in 1924 by dissolving acetate in acetone and using a dry spinning method. French company Rhône-Poulenc developed similar technology and established Rhodiaceta in 1922 to start industrial production of acetate fiber. Acetate also began to be used for cinematographic film in particular, and was not as flammable as nitrocellulose. Acetate fiber could not easily be dyed with normal cotton dyes, and so special synthetic dyes were developed for it. These disperse dyes were also later used for dyeing synthetic fibers. The production and utilization of acetate fiber necessitated the development of industrial organic chemical industries such as acetic anhydride and acetone, and also required far more advanced technology than viscose rayon, such as monoacetylation control technology, dry spinning, solvent recovery and dyeing with disperse dyes. Many of these technologies carried over into synthetic fibers.

(1) Acetate fiber

Since Japan had not significantly developed industrial organic chemicals prior to the Second World War, a number of companies prototyped acetate fiber in the 1930s and took it no further. Full-scale industrialization came in 1949. However, as this overlapped with the period of full-scale industrialization of synthetic fiber, acetate fiber was completely overshadowed by the development of synthetic fiber in Japan, and remained dormant, as shown in Fig. 4.4.

However, in the 1960s, acetate fiber was adopted as a raw material for cigarette filters, which were in widespread use in Japan. The demand for cigarette filters expanded in both the domestic market and the export market, and this industry, rather than clothing, remains the main use for acetate fiber. Unlike celluloid or rayon, acetate fiber has its own area of use that is not in competition with any petrochemical products, and its production volumes have continued to grow steadily. By the late 1990s, more than 100,000 tons were being produced; by the 2000s, production had even overtaken rayon fiber, as shown in Fig. 4.5.

(2) Acetate film

Another use for acetate other than fiber is photographic film. To ensure the fireproof properties of photographic film, there was a worldwide trend away from nitrocellulose film to acetate film. In 1948, Eastman Kodak successfully industrialized a fireproof triacetate film. Domestic production of triacetate film in Japan started in 1953. As early as the 1960s, a petrochemical product made an entry into this field in the form of PET film. However, PET film only went as far as X ray films, with triacetate film continuing to be used for ordinary photographic film. With the popularization of digital cameras from the late 1990s, production of ordinary photographic roll film rapidly declined in the 2000s, and the demand for triacetate photographic film decreased. However, from the 1990s onwards, triacetate film began to gain attention as a polarizing film for liquid crystal displays. Acetate film has thus survived as a new functional product.

4.1.5 Fine chemical products from cellulose

As cellulose polymers interact strongly through their hydroxyl groups, cellulose does not break down in water or organic solvents. If part of the hydroxyl group is esterized or etherized, the interaction between the polymers weakens, and they can break down in water or organic solvent. Various derivatives have been produced and used as fine chemicals. There are two main products of this type in particular, as follows.

Sodium carboxymethyl cellulose (CMC) is a polymer made by reacting cellulose treated with sodium hydroxide with monochloroacetic acid so the hydroxyl groups in the cellulose form carboxymethyl ether. The etherization makes the cellulose water soluble. CMC solutions are viscous, and form protective colloids. Once applied as a coating and dried, this forms a transparent film that has an adhesive effect. The solution is physiologically harmless, and is approved as a food additive both in Japan and overseas. Due to these characteristics, CMC has a wide range of uses, including as a dispersion stabilizer for food, a binder for pharmaceutical tablets, a wettable powder for pesticides and a surface sizing agent and internal strengthening agent for papermaking.

Methylcellulose is produced by reacting methyl chloride with cellulose treated with sodium hydroxide so some of the hydroxyl groups in the cellulose form methyl ether.

Unlike CMC, it is a nonionic cellulose ether. Since it is water-soluble and forms a viscous solution, its uses include an emulsion stabilizer and thickener in food and cosmetics, a protective colloid agent for thermal paper and a binder for pharmaceutical tablets.

4.2 Industrial organic chemicals and polymers from fermentation-based industrial organic chemical products

Industrial organic chemicals produced by fermentation process of carbohydrates include fermentation ethanol and fermentation acetone/butanol, as shown in Fig. 4.6. Production of ethanol and butanol as gasoline-substitute fuels and octane enhancers increased in many countries by national policy from the 1920s to the 1940s. As this resulted in an abundant supply, a number of chemical industries emerged using these as raw materials.

However, in the 1950s, as crude oil from the Middle East started being supplied in abundance to the rest of the world, the demand for fermentation ethanol as a fuel source decreased, and the fermentation-based industrial organic chemical industry lost its industrial base. Fermentation-based industrial organic chemicals and their derivatives were almost completely absorbed into petrochemical industry in the 1950s and the 1960s. Incidentally, the fermentation ethanol industry revived again in Brazil in the 1970s as a result of the oil crises, and once again experienced a sudden revival and subsequent development in the United States in the 2000s as an environmental countermeasure.

4.2.1 Fermentation ethanol

There have been industries for obtaining spirits with high ethanol concentrations by distilling fermented alcohol since before the modern era. However, many of these industries could not really be called chemical industries, as they used batch methods. The development of continuous distillation process turned fermentation ethanol into an industrial organic chemical industry.

(1) The start of ethanol fermentation in Japan

The military munitions factory imported Ilges-method distillation apparatus from Germany to produce solvents for making gunpowder, and was able to start production around 1902. This was the first introduction of continuous ethanol distillation apparatus to Japan.

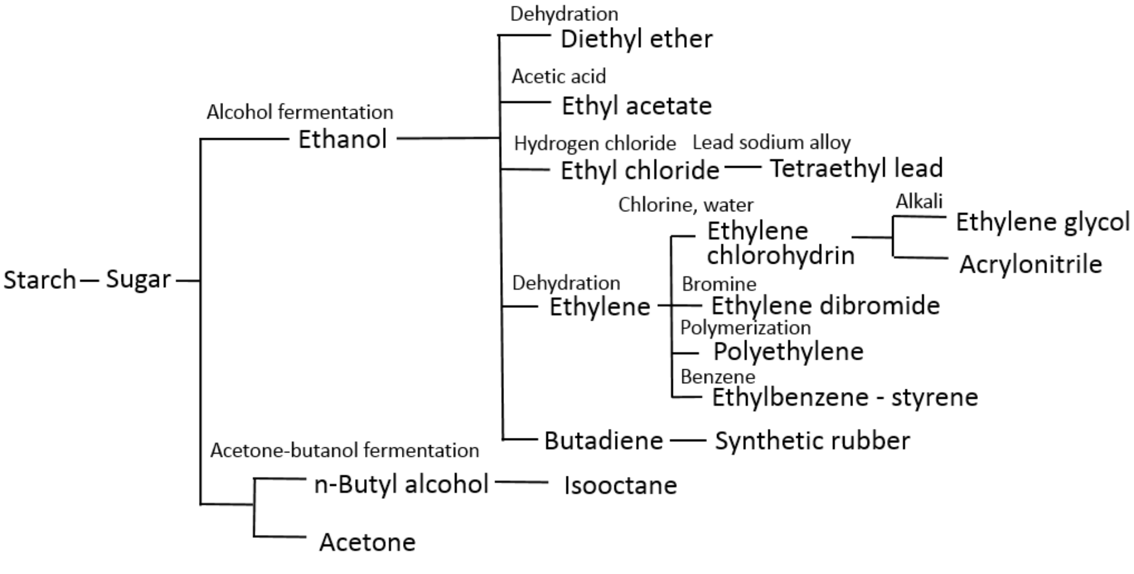


Fig. 4.6 Product categories of industrial organic chemicals as raw material produced by fermentation process.

Ilges-method distillation apparatus was made up of two distillation columns. The mash distillation column was made up of a baffle tray overlaid with a plate shaped like a gabled roof over the top of a parallel arrangement of slit holes. This was designed to prevent blockages, since the fermented mash had a lot of solid content. However, this equipment had poor distillation efficiency, as a lot of liquid would flow down through the slits. The crude ethanol obtained from the mash distillation column was refined in the rectifying column, comprising a regular bubble cap tray. The ethanol concentration after refining was around 92%.

Prompted by this introduction by the military munitions factory, Nihon Shusei Seizo also imported Ilges-method distillation apparatus and set up a factory in Asahikawa in 1902. The company had aimed to produce fermentation ethanol from potatoes, but it was disestablished the following year. However, similar attempts were made by Nippon Sugar Refining Company and other companies. By 1919, Guillaume-method apparatus, with an inclined mash distillation column, was also being imported; by 1920, there were 44 plants with Ilges-method distillation apparatus and 24 with Guillaume-method apparatus.

Alcohol tax was a major obstacle to using ethanol for non-liquor purposes. Accordingly, the government enacted the *Industrial Alcohol Tax Rebate Law* in 1906, not long after the introduction of Ilges-method distillation apparatus. This meant that the alcohol tax could be exempted for designated applications for the alcohol. For the first time, ethanol was recognized as a chemical substance that was distinct from liquor. The first 12 tax-exempt applications were designated in 1906: gunpowder (government and private sector), tobacco fermentation (government), varnish (private sector, also the following), ether, soap, tannic acid, borneol, vinegar, celluloid and its processing, perfume for export and steam engine fuel. These were successively added to until 1935. These designated applications provide a lot of detail on the uses of ethanol at that time; these are broadly categorized in Table 4.1. The most common applications were for solvents as product components, such as in perfume or collodion, for processing solvents, such as celluloid processing, or other solvents, such as extraction or precipitation solvents for digitalis extraction or diastase precipitation.

Ethanol has long been used as a raw material for industrial organic chemicals, such as for vinegar and diethyl ether. Vinegar accounted for around 20% of all ethanol usage, while ether accounted for around 10%, although consumption levels plateaued. Incidentally, from around 1933, there was an increasing growth in demand for ethanol as a raw material for ethers and other chemical compounds such as ethyl acetate, and the usage of ethanol for non-vinegar industrial organic chemicals rose to account for a quarter of all ethanol usage. Behind this, there are thought to be factors such as the domestic production of photographic film, and changes in varnish, lacquer and other coating products.

Table 4.1 Major use of ethanol specified in the industrial alcohol tax rebate law (1906 to 1935)

Category	Specific example
Solvent as a product component	Perfume, collodion, varnish, lacquer
Solvent for processing	Gunpowder, celluloid, faux coral beads, transparent soap, tobacco fermentation, photosensitive emulsion
Extraction solvent, precipitation solvent	Borneol, tannic acid-gallnut, diastase, vitamins, citronellol geraniol, hydro-sodium sulfite, digitalis preparations, organ preparations
Raw materials of chemical modification	Diethyl ether, vinegar, ethyl carbonate quinine, acetic acid, ethylene and its derivatives
Other	Fuel

(2) Petroleum-alternative fuel

With the First World War underlining the importance of petroleum, there began to be a growing interest in Europe in anhydrous alcohol as a fuel alternative to petroleum. In the 1930s, Germany, France, Italy and various other European countries enacted compulsory alcohol blending policies. Since ethanol forms an azeotrope with water at a concentration of 96%, the azeotrope (hydrous alcohol) obtained by ordinary distillation could be easily isolated even if the ethanol was mixed with gasoline. If it was made into anhydrous alcohol, it could be mixed at ratios of up to 20%. The anhydrous alcohol was produced by reacting the azeotrope with quicklime. Azeotropic distillation was developed around 1930, and anhydrous alcohol became more easily obtainable.

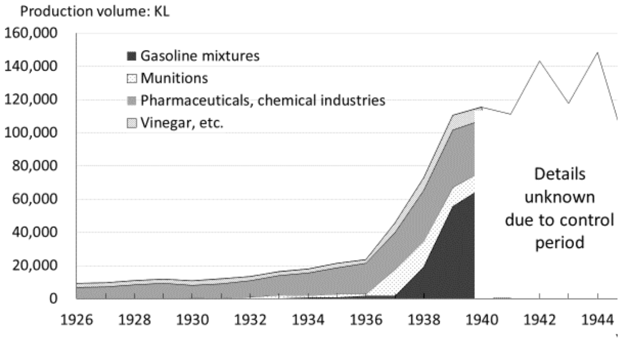
Azeotropic distillation was developed in Germany using the Drawinol process, which uses trichlorethylene, and in France using the Guinot process, which uses benzene or benzine. Distillation technology for fermentation ethanol had a significant impact on the development of cryogenic distillation technology by Linde, as mentioned in Section 2.3.2; this became a fundamental petrochemical technology. Similarly, azeotropic distillation technology to produce anhydrous alcohol also became an indispensable petrochemical technology.

In Japan, Ryūkichi Takahashi also developed an anhydrous alcohol azeotropic distillation process using trichlorethylene. Takahashi operated Takahashi Ironworks in Osaka, manufacturing boilers and chemical machinery. The Takahashi Ironworks mash distillation column comprised a bubble cap tray designed to prevent mash blockages. In 1934, Teikoku Seishu in Nagareyama, Chiba, started producing anhydrous alcohol (300 kL per year) using Takahashi Ironworks equipment. The following year, Showa Shuzo in Kawasaki started large-scale production (around 1,200 kL in 1935; around 4,500 kL in 1936; around 13,500 kL in 1937), also using Takahashi Ironworks equipment. Both companies were manufacturing synthetic sake from anhydrous alcohol. Showa Shuzo was a synthetic sake company founded by Chūji Suzuki for processing waste liquid from monosodium glutamate production. Synthetic sake was invented by Umetarō Suzuki of RIKEN in 1922, and was widely popularized by Showa Shuzo under the "Sanraku" brand. In 1939, Showa Shuzo established a new plant in Yatsushiro, Kumamoto, that was capable of an annual production of 18,000 kL.

The Japanese government enacted the *Alcohol Monopoly Law* and the *Volatile Oil and Alcohol Blending Law* in 1937, a little later than similar movements in Europe. These aimed to rapidly increase ethanol production for use as a fuel alternative to petroleum. Another aim was to rescue the flagging rural economy by increasing the production of tubers as raw materials for the ethanol. Under the *Alcohol Monopoly Law*, the production, import and sale of ethanol with a concentration of 90% or higher were all deemed to be state business, and state-run alcohol factories were established one after another from Hokkaido to Kyushu, using potatoes and sweet potatoes as raw materials. Thirteen factories were set up and running between 1938 and 1942. Most factories had an annual production capacity of 3,600 kL, while some had twice that at 7,200 kL. While these factories were a little larger in scale than many of the ethanol factories previously operated by private sake brewing companies, this was a far smaller scale than Showa Shuzo. Rather than the conventional fermentation technology of using malt to convert starch into sugar, which is then fermented using yeast, the state-run alcohol factories used amylo fungus for sugar conversion, then yeast for fermentation. The distillation apparatus was mainly Takahashi Ironworks equipment, the same as had been used by Showa Shuzo and other private companies. As a result of the enactment of the *Alcohol Monopoly Law*, the ethanol factories owned by private sake brewing companies were put under state-consigned production with the products supplied to the state; accordingly, freedom of operation became increasingly impossible.

The enacting of the *Alcohol Monopoly Law* and the *Volatile Oil and Alcohol Blending Law* significantly altered the demand volume for ethanol and the spectrum of its uses from 1937, as shown in Fig. 4.7. Rapid growth was seen in the use of ethanol for gasoline mixtures and for munitions. In 1935, the demand for fuel was less than 1,000 kL; this had risen to 19,000 kL by 1938 and to 66,000 kL by 1940. The breakdown of demand from 1941 to 1945 is unknown due to the controls in place at that time.

As the construction of state-run factories could not keep up with the growth in demand, a lot was being imported from Taiwan. Fermentation ethanol production in Taiwan also rapidly developed as a result of Japanese government directives and technical guidance. Since sugarcane was being used as a raw material for fermentation in Taiwan, production was more efficient, as it did not require the sugar conversion step in the process, required when tubers were used as a raw material. However, as wartime conditions intensified, marine transport became problematic; the volume of imports dropped rapidly from 1944 onwards. This was compensated for by increasing production at state-run factories and increasing the volume of production consignments to private sake companies.



Source: Ministry of Finance Tax Bureau Annual Statistics Report, Reference [11]

Fig. 4.7 Change of demand for usage of ethanol in the early Showa period.

(3) The development of chemical industries from fermentation ethanol

Figure 4.7 shows another area of growing demand for ethanol other than gasoline mixtures and munitions, namely, the demand for ethanol for chemical industries. It has already been mentioned that this demand started growing from around 1933. As an ample supply of fermentation ethanol became available from 1937 onwards, there was an increase in ethylene-based industrial organic chemicals that used it as a raw material. The demand for ethanol for chemical industries grew from 16,000 kL in 1935 to 35,000 kL in 1939. Ethylene was produced by dehydrating ethanol, as indicated in the product categories shown in Fig. 4.6. Ethylene can also be produced by partial hydrogenation of acetylene; however, this method also produces ethane, making the ethylene difficult to refine. Producing ethylene by dehydrating ethanol required a fixed-bed, vapor-phase, continuous reactor using a solid acid catalyst such as acid clay. Since ethylene and its halogen derivatives had already been designated under the *Industrial Alcohol Tax Rebate Law* in 1928, there is proof that ethylene was being produced in Japan from around this time.

Ethylene chlorohydrin, EG (a raw material for antifreeze) and ethylene dibromide (a scavenging agent for octane enhancers) were produced from ethylene. Tetraethyl lead (an octane enhancer) was also being produced on a large scale from ethanol via ethyl chloride. Ethylene chlorohydrin was also reacted with hydrogen cyanide to produce acrylonitrile, a raw material for oil-resistant synthetic rubber NBR. Antifreeze was used on the northern war front, and octane enhancers were indispensable in aviation fuel. Octane enhancers were used by mixing with scavenging agents, but up until just before the Second World War, these were all imported from the United States Ethyl Corporation. These industrial organic chemicals were all produced with domestic technology developed in absolute secrecy.

The system of products made from ethanol via ethylene, shown in Fig. 4.6, are far more highly specific than the system of petrochemicals discussed in the previous chapter, or the system of acetylene and coal tar products that shall be discussed later. The industrial organic chemical ethanol is used to produce the basic chemical product ethylene, which in turn can be used to produce new product categories. Calculating by theoretical product output level, since the product output level at the time is unknown, equivalent ethylene production estimated from the production volumes of EG and other ethylene products would have been 600–700 tons between 1940 and 1944. Ethylene and ethylene products were far smaller in scale than the equivalent ethylene production volume of 8,000–10,000 tons calculated from carbide/acetylene products (overwhelmingly, synthetic acetic acid), discussed later. However, assuming that all fermentation ethanol was made from ethylene, given the specificity of fermentation ethanol products, the equivalent ethylene production volume would have peaked at 60,000–70,000 tons in 1942, around 20,000 tons of which would have been used by chemical industries other than fuel or vinegar. Thus, the fermentation ethanol industry was a more significant chemical industry in the early 1940s than the carbide/acetylene industries.

(4) The decline and revival of the fermentation ethanol industry after the

Second World War

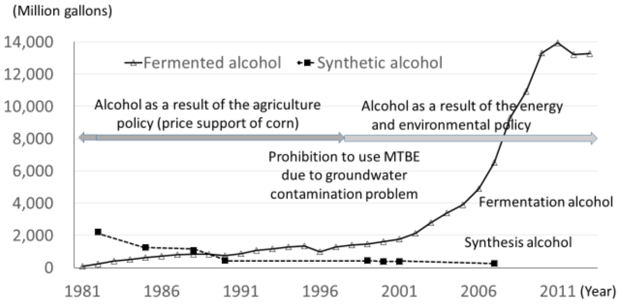
In Europe and Japan alike, the greatest demand for the chemical industries based on fermentation ethanol from the 1930s to the early 1940s was munitions. Consequently, once the war was over, there was no revival of the chemical industries based on fermentation ethanol. As the demand for gasoline substitute fuels also faded, for a long time fermentation ethanol production remained dormant.

The late 1960s saw the start of petrochemical ethanol (synthetic alcohol) production from ethylene in Japan. Within a short space of time, this had overtaken the fermentation process, supplying the demand for solvents, chemical raw materials, etc. However, the rising cost of petrochemistry resulting from the two oil crises, and the rapid increase in applications for food preservatives (food additives) [Footnote 1], which were monopolized by fermentation ethanol, sparked a revival of fermentation ethanol in the 1980s, turning the tables on the petrochemical method once more. Survival had been achieved by opening up areas of demand in which there was no competition from petrochemistry. Refining technology was licensed from French company Melle in the 1950s using the Allospas distillation process. This method involved adding water to already highly-concentrated ethanol and distilling it again. Adding water increased the relative volatilities of the ethanol and any impurities, thus making it easier to remove the impurities. This is called extractive distillation using water. Such technological improvements significantly lowered the amount of impurities (methanol, fusel oil, aldehydes) in the ethanol, meaning the growing demand in food product industries could be met by fermentation ethanol.

Most significantly, renewed cost competitiveness by dramatically altering the fermentation ethanol business also made a major contribution to the revival of fermentation ethanol in Japan. The industry started importing crude alcohol fermented and distilled overseas as a raw material, leaving only the refining to be done in Japan. As a result, there was a marked decrease in domestic fermentation.

Against this backdrop, the circumstances surrounding the fermentation ethanol industry worldwide completely changed after the oil crises, and a stable supply of crude alcohol became available. Brazil is the largest supplier of crude alcohol. In an attempt to rid itself of petroleum imports, Brazil started large-scale production of fermentation ethanol from sugarcane as a petroleum-alternative fuel right after the oil crises.

The United States started making extensive policies on alcohol additives to gasoline in the 2000s. This was a countermeasure for automobile emissions and a means of raising octane values. As Fig. 4.8 shows, these policies saw a rapid increase in the production of fermentation ethanol from maize in the United States within one short decade. Recent fermentation ethanol production volumes in the United States are more than six times higher than petrochemical ethanol production in the early 1980s. Production volumes in the 2010s have reached around three times those of Brazil.



Source: Fermentation process: The US Department of Energy, Energy Information Administration EIA
Synthetic process: Reference [37]

Fig. 4.8 Change of production volume of ethanol in the U.S.

Judging from equivalent ethylene (the amount of ethylene required calculated on the assumption that it was petrochemically synthesized from ethylene), production of fermentation ethanol in 2010 reached 25 million tons in the United States. An equivalent volume of ethylene was produced in the United States in 2012. From the 2000s, fermentation ethanol has made a rapid comeback for around a decade due to environmental policies.

[Footnote 1] All around the world, fermentation ethanol rather than petrochemical ethanol is used in vinegar, food preservatives, and other areas in which it may be absorbed into the human body.

4.2.2 Industrialization of polyethylene and polystyrene from fermentation ethanol

It has been noted in the history of Japanese petrochemical technology that LDPE and polystyrene made from fermentation ethanol started being produced domestically in Japan in 1944, towards the end of the Second World War, as there was a need for high-frequency insulating materials for radars. This is discussed in greater detail below.

It has now almost been forgotten that LDPE and polystyrene made from fermentation-ethanol-based ethylene was produced in Japan using Japanese technology. The military had a pressing need for these two new plastics at the time. However, this was a very small-scale demand, as the intended application was for insulating components for radars. Accordingly, although these plastics were industrialized, it was on a far smaller scale than the early industrialization in the petrochemical industry after the war. Since the industrialization took place towards the end of the war, there were concerns about a shortage of resources and raw materials. Ultimately, air raid damage meant the fledgling industry had to cede defeat after a short period of operation. Almost none of this technology was passed on, as the postwar industrialization was based on introduced technology. Nevertheless, this early industrialization using domestic technology indicates the heights reached by Japanese organic synthesis technology and polymer synthesis technology during the Second World War.

(1) Polyethylene

LDPE was invented in 1933 by British company ICI and industrialized in 1939, using fermentation ethanol as a raw material. Around 100 tons were produced in 1940, and its superior properties as a high-frequency insulating material were recognized. The Second World War had already begun; ICI supplied the technology to American company DuPont at the request of the United States Navy. In 1943, a plant with a 900 tons annual production capacity was built in the United States.

Meanwhile, Japan first became acquainted with LDPE in 1942 in the form of a radar cable captured from the American military. Domestic production of it became a pressing issue in Japan. Research began in the fall of 1943 by three groups commissioned by the navy through the Electrotechnical Laboratory. These were led by Prof. Yukichi Go of Osaka University and Mitsui Chemicals, Dr. Taizō Kume of the Noguchi Institute and Nippon Chisso Hiryō and Prof. Kodama Shinjirō of Kyoto University and Sumitomo Chemical.

The Noguchi Institute started experimenting in early 1944, with little literature to rely on, and, with astounding speed, had already established a manufacturing method using ethylene liquefaction and filling by summer that same year. In the summer of 1944, Nippon Chisso Hiryō (now Chisso) started construction on a plant at its factory in Minamata. Fit-out of the plant was completed by the end of December with a 1,000 atm compressor supplied by the navy fuel factory. Operation started successfully in early 1945, and by March the Noguchi Institute researchers were no longer needed. However, everything was completely destroyed in an air raid in May 1945. Following the Second World War, this domestic technology was completely buried.

In November 1944, Mitsui Chemicals started construction on a facility with a 20 kg monthly production capacity, but this ended without reaching production stage. In January 1944, Kyoto University started research with a 40 cc reactor, but this came to an end in March with only a small amount of specimens obtained. However, research began again after the Second World War, with Kyoto University taking on a commission from the Nippon Telegraph and Telephone Public. The university conducted a continuous industrialization experiment from 1951 to 1953 with a daily output of 10 kg, using fermentation ethanol as a raw material. Based on this research, Sumitomo Chemical used an industrialization testing subsidy from the Ministry of International Trade and Industry to build and operate an intermediate testing plant with a 3-ton monthly output capacity at its factory in Niihama in 1953.

This record of achievement made Sumitomo Chemical the company of choice when ICI was looking for a technology licensing partner in Japan.

(2) Polystyrene

A major challenge with polystyrene was coming up with a manufacturing method to produce the monomer styrene. German company IG Farben had started industrial production of styrene in the early 1930s using a method of dehydrogenating ethylbenzene with an alumina-chromia catalyst. Ethylbenzene was synthesized from ethylene and benzene using an aluminum chloride catalyst. This was a reaction often used in the oil refinery industry. However, the ethylbenzene dehydrogenation reaction had a low yield and produced tar as a byproduct. Accordingly, various alternative methods were developed.

During the Second World War, Japan industrialized styrene with three production methods using different raw materials, as shown in Fig. 4.9. These were the Hodogaya Chemical method, from ethanol via ethylene, ethylbenzene and 2-chloroethylbenzene; the Nihon Yuki method, from acetylene via acetophenone and α-phenyl ethyl alcohol (methyl phenyl carbinol); and the Shiono Kōryō method, by dehydrating rose perfume β-phenyl ethyl alcohol.

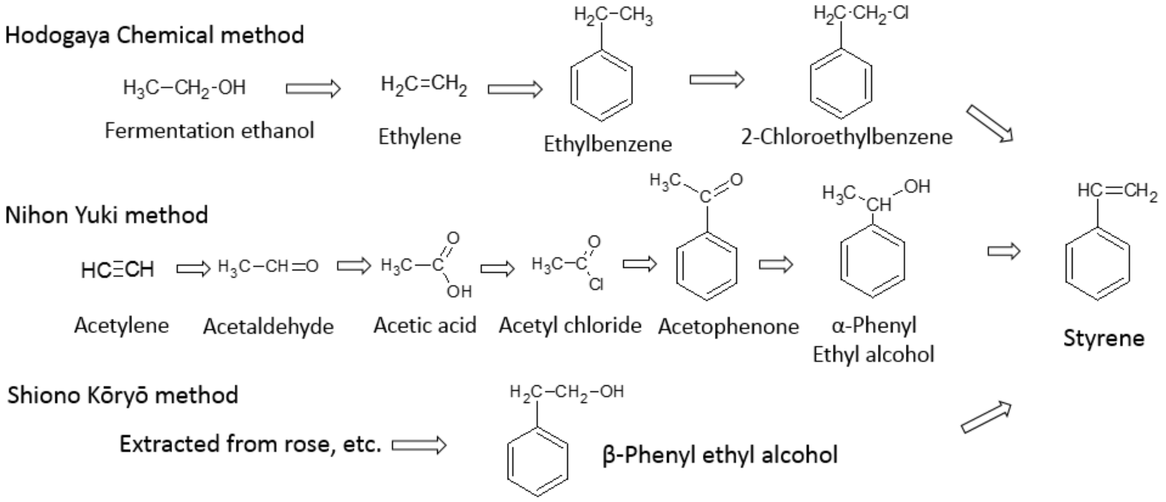


Fig. 4.9 Production method of styrene industrialized in Japan during the Second World War.

Hodogaya Chemical started research in 1938, with a request from the military to industrialize polystyrene. It came up with the alternative method of reacting chlorine with ethylbenzene to produce 2-chloroethylbenzene, which was dehydrochlorinated to form a styrene monomer. This method was deemed to have a higher yield than the IG Farben method. However, the polymerized polystyrene was brittle with a low molecular weight, and could not be made into a product. This was found to be caused by a secondary dehydrogenation reaction in the dehydrochlorination reaction process, producing traces of phenyl acetylene. This impurity was preventing the radical polymerization of the styrene. However, it was difficult to remove these trace amounts of impurities by distillation. Instead, the researchers at Hodogaya Chemical removed the acetylene-based impurities by exposing the styrene to an aqueous solution of copper, and then successfully synthesized high-molecular-weight, low-dielectric-loss polystyrene. Care had to be taken with the generation of copper (I) acetylide, as there is a risk of explosion when handling acetylene-based compounds. This was a superb piece of refining technology, using this to the opposite effect. This indicates the level of analysis technology and organic synthesis technology Japanese chemical companies had at the time. A year of industrialization experimentation took place from the fall of 1941; by the fall of 1942, production technology had been completed to produce polystyrene from ethanol via ethylene. However, there was a shortage of resources and the construction of plants took longer than anticipated; a plant with a 5-ton monthly production capacity was finally completed in August 1944 in Komatsugawa, Tokyo. The factory started out operating well, but was damaged by a fire in January 1945 and an air raid in March, and was never able to reopen.

Nihon Yuki, a joint venture between Kao Sekken Nagase Shokai and Tekkosha, was established in 1940 with polystyrene production as one of its aims. The Tekkosha factory at Sakata produced acetic acid, and subsequently acetyl chloride, from acetylene via acetaldehyde. The acetyl chloride was reacted with benzene to produce acetophenone, which was transported to the Nihon Yuki factory at Hirai, Tokyo. The acetophenone was then high-pressure hydrogenated to produce α-phenyl ethyl alcohol. The high-pressure hydrogenation technology had been mastered by Kao Sekken for producing higher alcohols from fats and oils. The α-phneyl ethyl alcohol was then dehydrated to produce styrene, which was then made into polystyrene. Operations started in 1944, producing 12 tons by 1945. However, the plant was hit by an air raid in March 1945, and was unable to reopen.

Shiono Kōryō is a perfume and fragrance company in Mikuni, Osaka, with a history of extracting and producing natural perfumes and fragrances. The company developed its own technology to obtain styrene by dehydrating the β-phenyl ethyl alcohol fragrance found in roses and other flowers, and then independently developed the technology to produce polystyrene from this. Designated as a polystyrene supplier by the Ministry of Munitions in 1944, the company produced around 1 ton a month, although it had a 2 tons monthly production capacity. This invention was a commendable idea that turned the tables on the wartime slump in the perfume and fragrance business.

4.2.3 Fermentation acetone/butanol

Louis Pasteur discovered that butanol could be made from anaerobic bacteria. Chaim Weizmann of the University of Manchester (later the first president of Israel) isolated a potent strain of bacteria in 1912, and patented an acetone/butanol production method using this strain in 1915. This fermentation process was industrialized in the United Kingdom and Canada during the First World War, as acetone was needed for making gunpowder. In 1920, DuPont invented nitrocellulose coating, which used butyl acetate as a solvent; this resulted in large-scale acetone/butanol fermentation in the United States as well. In 1931, Koei (now Koei Chemical Company) started industrial production in Japan as well. Sucrose was used as the raw material.

In 1936, three companies (Godo Shusei, Takara Shuzo and Dai Nippon Shurui Seizo) jointly established a research institute, and started researching isooctane aviation fuel from butanol [Footnote 2]. This led to the establishment of Kyowa Hakko Kogyo after the war. The research gained the attention and support of the Imperial Japanese Army Air Service. At the end of 1940, an isooctane sample was presented to the army, and the Air Service headquarters urged industrial production. As a result, a pilot plant was built at the Godo Shusei factory in Asahikawa, which had already been working on acetone/butanol fermentation. Unlike fermentation ethanol, fermentation acetone/butanol research and production was spearheaded by private companies.

At the start of the Pacific War, the government was inclined towards isooctane production from fermentation butanol, as it had annexed regions to the south with a ready supply of sucrose. As a result, the Toyobo factory in Hofu was converted over to the production of acetone/butanol and isooctane in 1943. A large-scale, 400 kL fermenter was constructed at the Hofu factory, and butanol production started at the end of 1943.

[Footnote 2] n-butanol is dehydrated to produce n-butylene, which is then isomerized to produce isobutylene. The isobutylene is dimerized and reduced further to produce isooctane. A method of reacting isobutylene with isobutane to produce isooctane was also known at the time.

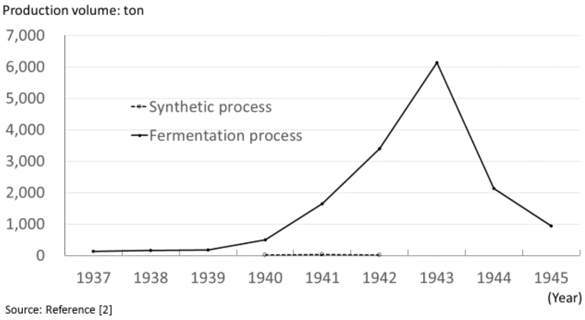


Fig. 4.10 Production volume of butanol in Japan during the Second World War.

However, with the wartime situation intensifying in 1944, it was no longer possible to ensure possession of the regions in the south, which made it difficult to obtain sucrose. The government issued instructions for the factory in Hofu to suspend production of isooctane and switch from acetone/butanol to producing anhydrous alcohol from tubers. Accordingly, the factory in Hofu continued anhydrous alcohol production from 1944 until the end of the war.

Butanol can also be produced from carbide/acetylene. However, synthetic butanol production stopped at the trial production stage, as shown in Fig. 4.10, and the butanol supply was almost entirely provided for by fermentation process.

Right after the end of the war, the managers and operators of the Hofu factory devised a plan to resume production of acetone/butanol from cheap, imported molasses instead of sucrose. Although the permit to import the molasses took more than two years from the time of application, it was finally granted in 1948. After several years, the fermentation process overtook the carbide/acetylene synthesis method resumed shortly after the war.

The demand for butanol rapidly increased as a raw material for polyvinyl chloride plasticizers DBP and DOP. This resulted in a rapid postwar revival of fermentation acetone/butanol, unlike fermentation ethanol. This situation continued until the advent of the petrochemical method in 1962. In the early 1960s, the fermentation process accounted for 27,000 tons of butanol per year, while the carbide/acetylene synthesis method accounted for no more than 6,000 tons per year.

However, with plans afoot for transitioning to petrochemical methods, the price of acetone and butanol began to drop from the late 1950s onwards, with the expectation that the cost of petrochemical production would decrease. Accordingly, fermentation companies and acetylene synthesis companies alike abandoned their existing facilities and quickly started shifting to petrochemistry. As a result, fermentation process production came to a halt within two years of the start of the petrochemical method. Unlike fermentation ethanol, fermentation acetone/butanol has not continued anywhere in the world to the present day.

4.3 Industrial organic chemicals and polymers from fats and oils

The main chemical products made from fats and oils that have existed since before the modern chemical industry are soap and coating. Soap has been produced since ancient times by boiling fats and oils in alkalis.

Coatings have also been made since ancient times by mixing pigments with drying oil (oils containing large numbers of unsaturated bonds, such as linseed oil or tung oil) or semi-drying oil (such as soybean oil). The unsaturated bonds in the oil are oxidized by the oxygen in the air and polymerize, thus resulting in a weather-resistant polymer product. While not an oil, Urushi lacquer has similarly been made since ancient times in Japan and East Asia using an air oxidation polymerization process. One drawback with these coatings is that they were very slow to dry (polymerize) once applied. In order to quicken the drying (polymerization) process slightly, the oil was mixed with lead, manganese, or cobalt oxide and then boiled.

With the development of oleochemistry in the 20th century came the production of a number of industrial organic chemicals and polymers from fats and oils, as shown in Fig. 4.11.

4.3.1 Soap/hydrogenated oil

Soap took hold in Japan as an imported product in the early Meiji Period. A number of newcomers appeared in the market, expecting the demand to grow, and technology was introduced from the West. However, this never grew beyond the domain of handicrafts using open-fire saponification kettles and mold-kneading technology.

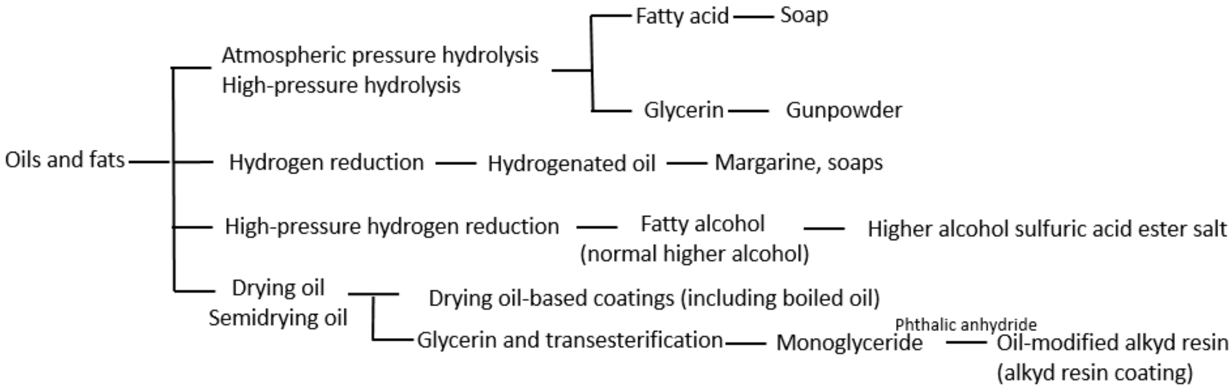


Fig. 4.11 Product categories of fats and oils as raw materials.

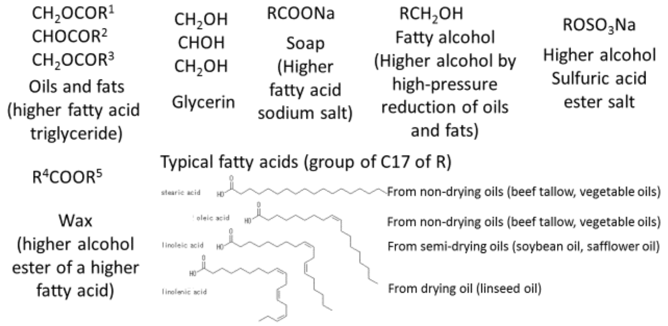
The Japanese soap industry became established as a modern chemical industry around 1900. Nagase Shokai (now Kao) advocated the production of high-quality soap and set up factory production facilities, introducing steam saponification kettles and machine mixing technology. In 1910, the company started production of high-purity fatty acids and glycerin by high pressure hydrolysis of fats and oils using autoclave equipment imported from Germany. This made it possible to produce good quality soap.

Up until the First World War, all glycerin had been imported. In 1911, Nagase Shokai started recovering crude glycerin from the liquid waste from its soap, and many other companies followed suit. Refined glycerin was needed by the military for gunpowder, and so glycerin became subject to the *Law Promoting the Production of Dyes and Pharmaceuticals* (1915). Based on this law, the national policy concern Nippon Glycerin was established in 1916 with a capital stock of ¥6 million to produce refined glycerin.

Around the same time, hydrogenated oil began being produced by hydrogenating fats and oils. At the time, there was an abundant supply of fish oil (sardine oil, etc.). Since fish oil contains a lot of unsaturated fatty acids, it would form solid hydrogenated oil at normal temperatures when hydrogenated with a nickel catalyst. The hydrogenated oil was used as a substitute for the imported beef tallow used for making soap.

4.3.2 Expansion into diversified oleochemistry

In the 1930s, companies started moving away from the soap/ fats and oils industries and into diversified oleochemistry. For reference, Fig. 4.12 shows the chemical structures of the fats and oils and fat and oil products discussed below, as it is difficult to explain the developments in oleochemistry using words alone. In the early 1930s, synthetic surfactant higher alcohol sulfuric acid ester salt (AS) (see Section 3.4.7 (2)) was imported for the first time from Boehme in Germany. While this surfactant is still used as a neutral detergent for washing high-end garments, etc., at the time it was used more as a dyeing auxiliary for helping dyes permeate and adhere uniformly to fabric than for laundry. This product spurred Japan into initiatives to produce its own higher alcohol sulfuric acid ester salt.



Note: R^1 to R^5 contain 1 to 3 of long, linear alkyl groups or double bonds.
Many have an odd carbon number between 11 to 21.

Fig. 4.12 Major molecular structures of oleochemistry products.

Dai-ichi Kogyo Seiyaku used sperm whale oil (spermaceti) as a raw material. The main component in spermaceti is a wax (higher alcohol ester of a higher fatty acid) rather than an oil (higher fatty acid triglyceride). Specifically, it is the ester of palmitic acid and cetyl alcohol. Consequently, it produces a higher alcohol (mainly cetyl alcohol) when hydrolyzed, and esterizes with sulfuric acid. Dai-ichi Kogyo Seiyaku developed this production technology in 1934, and started production in 1938. It was first marketed as the household neutral detergent "Monogen," safe on wool and other delicate fabrics. This was the first synthetic detergent produced with Japanese technology. However, high pressure hydrolysis technology was introduced in the 1910s that could extract the cetyl alcohol from spermaceti. Since it is a wax rather than an oil, the higher alcohol could be obtained by high pressure hydrolysis.

Kao used high-pressure reduction of coconut oil to produce a higher alcohol, which was then subjected to sulfuric acid esterification and marketed as the synthetic detergent "Exceline" in 1938. Kao's technology reduced the higher fatty acid using hydrogen at high pressure. High-pressure reduction technology had a broad range of applications, and marked the beginnings of diversified oleochemistry. In 1939, Kao successfully produced an aircraft lubricant by reducing a higher fatty acid at high temperature and pressure using a zinc catalyst to obtain α-olefins, which were then oligomerized with aluminum chloride. In 1940, the United States started imposing high-octane gasoline and aircraft lubricant embargoes on Japan. At the request of the military, at the end of 1941, Kao started construction of an aircraft lubricant factory with an annual production capacity of 100 kL. High-pressure reduction technology was also used in the production of sorbitol from glucose (industrialized in 1943), and α-phenyl ethyl alcohol from acetophenone (raw material for styrene, mentioned in Section 4.2.2 (2), industrialized in 1943).

The production of one particular higher alcohol by high-pressure reduction of fats and oils contributed to the postwar revival of the oleochemical industry. This was n-octyl alcohol for the plasticizer DOP, used in PVC. However, straight-chain octyl alcohol from fats and oils was not as good a plasticizer as branched-chain octyl alcohol synthesized from acetylene/acetaldehyde, and the later growth in plasticizers was through the acetaldehyde method.

The emergence and subsequent significant development of synthetic detergents from petrochemical products in the 1950s–1960s placed significant pressure on soap and synthetic detergents made from fats and oils. However, the early rapid growth in synthetic petrochemical detergents was accompanied by some environmental issues (foam pollution in rivers) in the 1960s, both in Japan and in the West. The cause of this was investigated, followed by initiatives to "soften" synthetic detergents [Footnote 3]. Environmentally biodegradable surfactants began to be produced from straight-chain higher alcohols and straight-chain α-olefins using fat and oil high-pressure reduction technology. The synthetic detergent "softening" process only took six years in Japan, and was fully completed in the early 1970s. This process was accompanied by a revival in large-scale production of higher fatty acids and higher alcohols from fats and oils. Diversified oleochemistry joined with petrochemistry to expand in new directions.

4.3.3 Oil-modified alkyd resin

An alternative to the drying-oil coatings that have been used since ancient times is nitrocellulose coating, made up of nitrocellulose and an organic solvent. Due to its quick drying time, this coating suddenly grew in popularity in the 1920s, alongside the flourishing American automotive industry.

Oil continued to be used in coating, thanks to the development of oil-modified alkyd resin in the late 1920s, made from drying oil, semi-drying oil and phthalic anhydride. When oil (higher fatty acid triglyceride) reacts with glycerin, transesterification occurs, producing a mix of higher fatty acid monoglycerides and

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[Footnote 3] Detergents with poor environmental biodegradability are termed "hard," while those with good biodegradability are termed "soft."

diglycerides [Footnote 4], as shown in Fig. 4.13. When this reacts with phthalic anhydride, the monoglyceride molecules, which have two hydroxy groups, form several bonds (oligomerization). The diglycerides, which only have one hydroxy group, stop the bonds from extending, thereby regulating the length of the oligomer molecules. Since the unsaturated bonds contained in the higher fatty acid remain as they are, as indicated by R^1 and R^2 in Fig. 4.13, once the coating has been applied, oxidative polymerization occurs through contact with the oxygen in the air, similar to drying-oil coatings. This is shown in Fig. 4.13 as alkyd resin.

Since the alkyd resin has more unsaturated bonds per oligomer molecule than the original unsaturated oil, it dries faster and is also more weather-resistant and more flexible. Like boiled oil, alkyd resin dries even faster when combined with cobalt naphthenate, lead naphthenate, or other additives. Alkyd resin has been produced domestically in Japan since the start of the 1930s, and is also known as phthalic acid resin.

After the war, a mixture of alkyd resin and amino resin (butylated melamine formaldehyde resin, butylated urea formaldehyde resin, etc.) emerged in 1948 in the form of amino-alkyd resin baked coating. However, as the petrochemical industry moved into domestic production and expansion, a number of petrochemical polymers began to be used in coatings, significantly reducing the role played by oil-based coatings. Amidst such trends, however, some products, such as epoxy alkyd resin coating, are still being produced that utilize the strengths of both petrochemical and oil-based coatings.

4.3.4 Biodiesel oil

There have been significant changes in the directions taken in oleochemistry in recent years. Policies such as the Biofuels Directive issued by the EU in 2003 have aimed to accelerate the use of renewable resources in order to reduce greenhouse gases. One such example is the rapid increase in production of fermentation ethanol in the United States, discussed previously. These initiatives have even extended as far as fats and oils. Europe has seen a rapid increase in the use of biodiesel oil from palm oil, rapeseed oil, sunflower oil and other such sources. Biodiesel oil is a higher fatty acid methyl ester produced by the transesterification of oil (higher fatty acid triglyceride) and methanol. Technically, it only refers to product that has already been used in the course of higher alcohol production. However, biodiesel oil production has increased dramatically due to its use as an automotive fuel, with the production of palm oil rapidly increasing from 300,000 tons in 1995 to 41 million tons in 2009.

[Footnote 4] The molecular structure of glycerin is $CH_2OH – CHOH – CH_2OH$. Oil (higher fatty acid triglyceride) has a molecular structure of $CH_2OCOR^1 – CHOR^2 – CH_2OR^3$, where R represents the alkyl group. When the glycerin and oil are transesterified, one or two alkyl groups in the oil break away to form hydroxy groups OH. These are called diglycerides and monoglycerides.

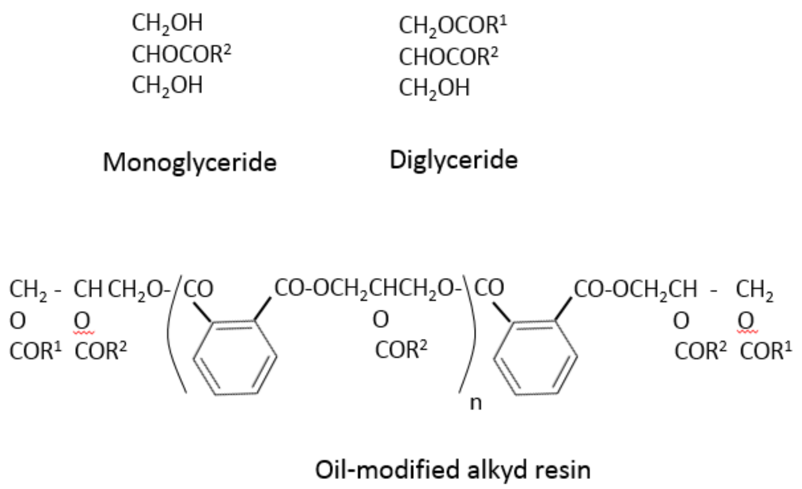


Fig. 4.13 Molecular structures of glycerides and oil-modified alkyd resin.

4.4 Industrial organic chemicals and polymers from coal

Coal chemistry, or the forest of products made from coal, flourished for a long time before and after the advent of petrochemistry. Coal chemistry falls into three broad categories, each of which has developed so significantly that it has been assigned a separate section here. These separate forests are carbide/acetylene chemistry, coal tar/aromatic chemistry and coke/syngas chemistry.

Another such forest was the use of gas (called coke oven gas or coal gas) produced in the dry distillation of coal chemicals. The main components in coke oven gas are hydrogen and carbon monoxide; these were widely used in city gas supplies, as well as providing the raw material by which the ammonia industry was established. Coke oven gas also contains various other substances in addition to hydrogen and carbon monoxide, including ammonia, sulfur compounds and hydrocarbons – including ethylene. It is difficult to extract and refine the ethylene from coke oven gas to use it as a raw material for industrial organic chemicals, and this was largely not done in Japan. However, it was done in Germany, and in wartime it ranked among the most significant sources of ethylene next to dehydration of fermentation ethanol and partial hydrogenation of acetylene; it was also a source of EG and other such substances. The coke oven gas forest is not a significant one in terms of industrial organic chemicals, and no further details have been included here.

4.5 Industrial organic chemicals and polymers from carbide/acetylene

Carbides are made from coke, produced by distilling coal, and as such are one of the forests of petrochemistry. Carbides are produced by reacting coke with quicklime in an electric furnace at a temperature of 2,000°C or higher. This requires a lot of electricity and can also be counted as an electrochemical industry.

Lime nitrogen is produced by exposing carbides to a nitrogen flow at 1,000–1,100°C. Lime nitrogen on its own is used as a nitrogenous fertilizer. Since it produces ammonia when reacted with steam, it can also be absorbed into sulfuric acid and then used as a nitrogenous fertilizer in ammonium sulfate form (converted ammonium sulfate) [Footnote 5]. When carbides react with water at normal temperatures, acetylene is produced. This reaction was discovered in 1862 by German chemist Friedrich Wöhler, one of the founders of organic chemistry.

While lime nitrogen was industrialized

[Footnote 5] Ammonium sulfate (ammonium sulfate fertilizer) made from ammonia produced directly from nitrogen and hydrogen is called synthetic ammonium sulfate. By contrast, ammonium sulfate made from ammonia produced by reacting lime nitrogen with steam is called converted ammonium sulfate. Ammonium sulfate produced in the treatment of waste sulfuric acid from the production of caprolactam or other chemical compounds other than ammonium sulfate is called recovered ammonium sulfate, while ammonium sulfate made from ammonia found in coke-oven gas generated in coal carbonization is called byproduct ammonium sulfate.

several years after the industrialization of carbides, the acetylene chemical industry was not established until the 20th century, around 50 years after Wöhler's discovery.

4.5.1 Carbides

Carbides were industrialized by American company Union Carbide in 1894, and around the same time in Europe. Acetylene was initially used as acetylene gas for lighting. One useful application that was developed was safety lamps for mineshafts. Later, a number of improvements were made to carbide production, including shifting the electric furnaces from single-phase to three-phase current, and changing the carbon source from charcoal to anthracite and then coke. By 1915, 10,000 kW large-scale electric furnaces were being built.

Lime nitrogen formation was discovered in Germany in 1897. Later furnace improvements resulted in the industrialization of the Frank-Caro furnace in 1908. This made it possible to produce large volumes of nitrous fertilizer from the nitrogen in the air, as well as ammonia, and lime nitrogen / converted ammonium sulfate plants began to be established all around the world, such as the American Cyanamid Company at Niagara Falls in the United States in 1909.

In Japan, Tsuneichi Fujiyama and Shitagau Noguchi successfully produced carbides with a 50 kW electric furnace in Sankyozawa, Sendai, in 1902. Later, Noguchi established Nippon Chisso Hiryō (now JNC), and in 1908 built a plant in Minamata with four German-made 3,000 kW carbide furnaces, and started producing lime nitrogen. Meanwhile, Fujiyama established Hokkai Carbide Plant (now Denka) in Tomakomai in 1912. He established a plant in Ōmuta, Fukuoka, in 1916, and another in Ōmi, Niigata, in 1921, significantly expanding the carbide, lime nitrogen and converted ammonium sulfate industries.

Up until around 1950, 50–80% of carbides were used for fertilizer, and 20–30% were used for lighting, welding and cutting, as shown in Fig. 4.14.

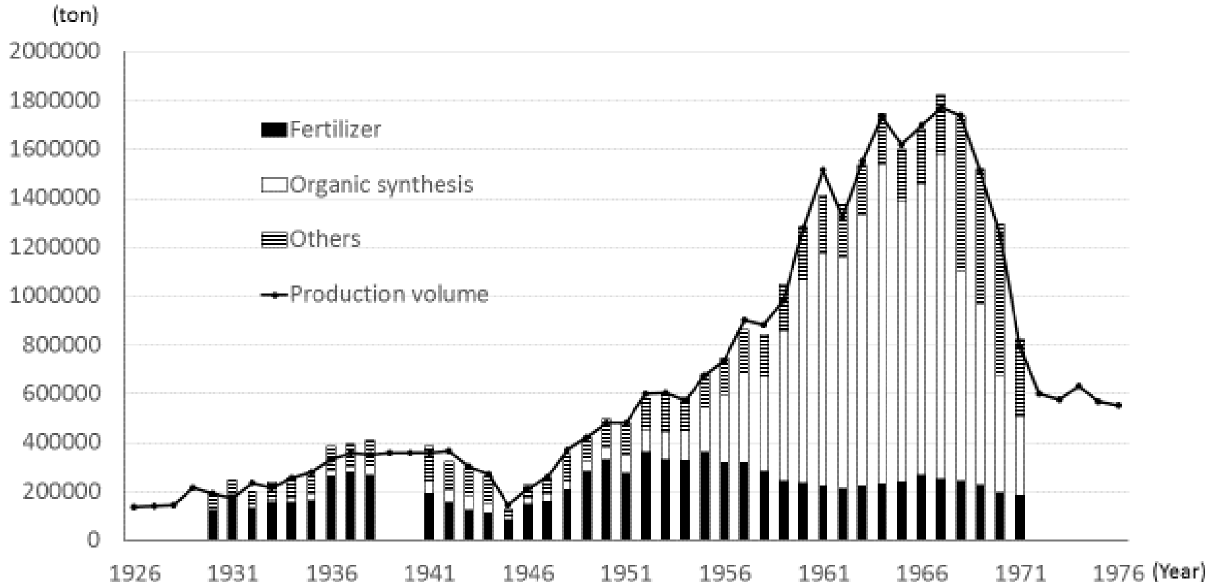
The process of directly synthesizing ammonia from nitrogen and hydrogen was industrialized in 1911 by German company BASF. This technology provided some competition for the method of manufacturing nitrogenous fertilizer from carbides. Direct ammonia synthesis spread around the world in the 1920s, with a succession of Japanese companies also entering the direct ammonia synthesis market and producing synthetic ammonium sulfate in the 1920s and the 1930s, following its industrialization in 1923 in Nobeoka (now Asahi Kasei) by Nippon Chisso Hiryō using the Casale method from Italy. However, even the emergence of synthetic ammonium sulfate did not result in a dramatic decrease in demand for carbides for fertilizer. After the Second World War, there was a call to increase fertilizer production, and the carbide industry quickly revived in response.

A detailed examination of carbide consumption reveals that from the 1950s onwards, there was a decrease in carbide use for fertilizer as the main area of demand, replaced by a rapid increase in its usage in the acetylene chemical industry. However, acetylene chemistry came under pressure from petrochemistry in the 1960s, and had almost disappeared by the end of the decade. Carbide production peaked in 1965 and rapidly declined after that.

4.5.2 Acetylene chemical industry

The acetylene chemical industry based on acetylene made from carbides was founded in 1916 by German company Wacker, with the production of acetyl aldehyde by reacting acetylene and water. Many companies soon entered the market in Germany, Canada and the United States, resulting in the demise of the wood carbonization industry, as mentioned in Section 4.1.1.

In Japan, the Nippon Synthetic Chemical Industry started producing acetaldehyde in 1928 as an intermediate for synthetic acetic acid production. The acetylene chemical industry continued to expand in Japan for another 40 years. Up until the 1950s, the Japanese acetylene chemical industry mainly revolved around the production of acetaldehyde and synthetic acetic acid. During these two decades, organic synthesis (the acetylene chemical industry) accounted for around 10% of all carbide consumption, other than during the Second World War, as shown in Fig. 4.14.



Source: Reference [25] (for 1926 to 1960), chemical industry statistics by Ministry of International Trade and Industry (for 1961 to 1970), and consumption detail statistics have not been released (from 1972)

Fig. 4.14 Change of production volume and demand detail of calcium carbide.

The 1950s and the 1960s, however, saw a sudden increase in organic synthesis. This meant an accompanying rapid increase in carbide production, far exceeding peak prewar volumes. The main reason for this increase was vinyl chloride, which was solely used for making PVC. Acetylene chemistry also rapidly expanded in scale, with growing demand for monomers and polymers. Vinyl acetate, chlorine-based solvents and many other industrial organic chemicals were also produced from acetylene, as shown in Fig. 4.15.

However, carbide production volumes dropped rapidly at the end of the 1960s. The main reason for this was also organic synthesis. With the production of acetaldehyde, vinyl chloride and nearly every other industrial organic chemical made from acetylene changing over to petrochemical methods, the acetylene chemical industry fell into rapid decline. The main reasons for this were the rising cost of electricity, which meant that carbide-based acetylene could no longer compete with basic petrochemicals, as well as the fact that a succession of low-cost production methods were being developed for producing industrial organic chemicals from basic petrochemicals, such as the Hoechst-Wacker process and the oxychlorination process.

Below, we shall discuss the main products and technologies of the acetylene chemical industry, as well as the industry policies aimed at boosting industrial organic chemical industries just before the Second World War in Japan.

(1) Acetaldehyde

Acetic acid and acetone were supplied by the wood carbonization industry from the late 19th century onwards. As mentioned previously, acetylene-based acetaldehyde was industrialized by German company Wacker during the First World War. Since acetic acid could be produced cheaply from acetaldehyde using manganese acetate as a catalyst, Germany started exporting synthetic acetic acid around the world after the war, putting the wood carbonization industry at risk of disappearing. Japan also investigated the domestic production of synthetic acetic acid, and several negotiations were made with German company IG Farben over technology licensing. However, a compromise on the conditions could not be met, so the four companies of the Dai Nippon Acetic Acid Manufacturers' Association started jointly researching under the supervision of the Osaka Municipal Technical Research

Institute and sharing their results. Their industrialization experiments ended in 1927. That same year, the four companies jointly funded the establishment of Nippon Gohsei Kagaku Kenkyusho (now The Nippon Synthetic Chemical Industry). Since carbides were needed as a raw material, a factory was constructed in Ogaki on a site adjoining carbide manufacturer Ibigawa Electricity Company (now Ibiden), and production started in 1928, with an output of 60 tons per month. The lifting of the gold export embargo in 1930 increased imports of synthetic acetic acid, synthetic methanol and other imports, prompting the four companies financing The Nippon Synthetic Chemical Industry to rapidly reduce their own wood carbonization operations and instead boost the synthetic acetic acid production capacity of The Nippon Synthetic Chemical Industry.

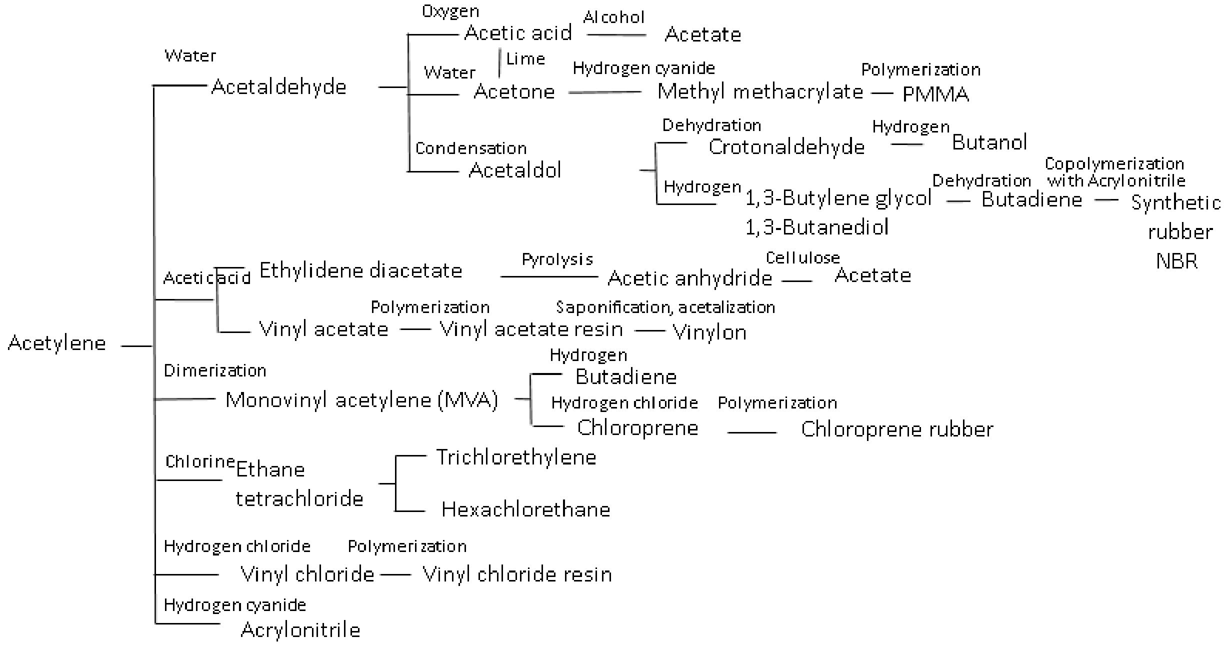
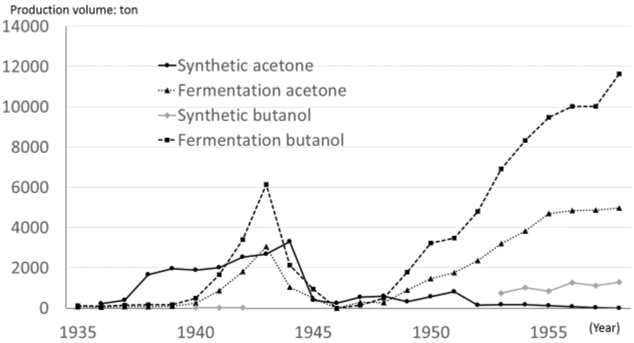


Fig. 4.15 Product categories industrialized using acetylene as raw material in Japan.

Acetaldehyde, via acetic acid, was used to produce acetone using lime acetate pyrolysis. It was also possible to make butanol by aldol condensing acetaldehyde in the presence of an alkali catalyst, then dehydrating it to produce croton aldehyde $CH_3CH=CHCHO$, and then hydrogenating this to produce butanol. The Nippon Synthetic Chemical Industry constructed a factory in Uto, Kumamoto, in 1939 as a production base for integrated acetone and butanol production from carbides. This factory directly synthesized its acetone from acetylene and large quantities of steam using iron oxide or zinc oxide as a catalyst, rather than from acetaldehyde and acetic acid. This process produced hydrogen and carbon dioxide as byproducts. However, the start of acetone/butanol fermentation from sucrose in the 1940s and molasses in the 1950s saw the fermentation process overtake and dominate the acetylene synthesis method, as shown in Fig. 4.16 (see Section 4.2.3). Initially, there were no other significant industrial organic chemicals made from acetylene except for acetaldehyde and acetic acid.



Source: Reference [2]

Fig. 4.16 Change in production volume of acetone and butanol from the 1930s to the 1950s.

(2) The *Organic Synthesis Industry Law*

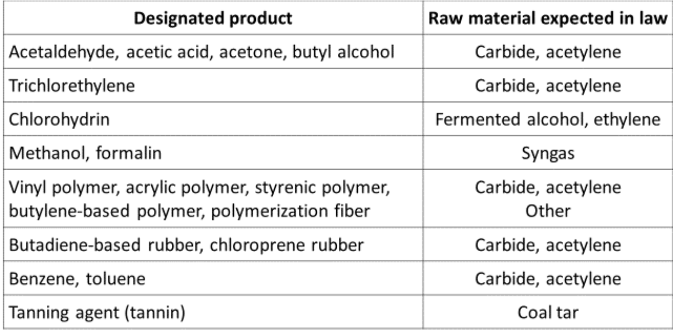
The large-scale industrial organic

chemical industry and synthetic polymer industry underwent significant expansion in Japan from the late 1930s, when the wartime economy system came into force. This can be seen in laws such as the *Artificial Petroleum Production Industry Law* and *Alcohol Monopoly Law* of 1937 and the *Organic Synthesis Industry Law* of 1940. The *Artificial Petroleum Production Industry Law* aimed to promote the synthesis of petroleum from coal as a national policy. This is discussed later in the section on products made from syngas (Section 4.7.2). The *Alcohol Monopoly Law* promoted the rapid increased production of fermentation anhydrous ethanol for a petroleum fuel alternative as a national policy, as discussed in Section 4.2.1.

The *Organic Synthesis Industry Law* aimed for the rapid expansion of organic synthesis businesses. Therefore, while free entry into the main organic synthesis businesses was restricted by government licensing, license holders were given special protection, such as commercial code exemptions in relation to issuing corporate bonds, land expropriation rights as needed, import restrictions on goods that could hinder the establishment of business and manufacturing incentive grants. Organic synthesis businesses essential to the defense industry (synthetic rubber, synthetic toluene, etc.) were given additional protection measures, such as exemptions from income tax and sales tax for certain periods, exemptions from import tax on necessary imported machinery and testing and research incentives.

Under the *Organic Synthesis Industry Law*, production expansion or urgent commercialization was deemed necessary for 18 designated industrial organic chemical or polymer products (Table 4.2). Many of these were industrial organic chemicals or polymers made from carbide/acetylene. Of these, the products that could still be classified as being industrially produced from carbide/acetylene by 1945 were acetaldehyde, acetic acid, acetic acid ester, acetone, vinyl acetate (vinyl acetate resin), acetic anhydride (acetate), trichloroethylene, vinyl chloride (PVC), methyl methacrylate (methacrylate resin) and polystyrene. Besides these, chlorohydrin was also being produced from ethanol via ethylene, and small volumes of polystyrene were also being produced from ethanol and the fragrance β-phenylethyl alcohol, besides from acetylene, as discussed previously. Synthetic rubber will be discussed in the following section. Methanol was being produced from syngas since before the *Organic Synthesis Industry Law* was enacted. Synthetic tannin was industrialized by Nitta Chemical, Nihon Kasei (now Mitsubishi Chemical) and Mitsui Chemicals. Mitsui Chemicals used spent sulfite liquor as a raw material in its manufacturing process.

Table 4.2 Eighteen products designated by the Organic Synthesis Industry Law in January 1941



Designated product	Raw material expected in law
Acetaldehyde, acetic acid, acetone, butyl alcohol	Carbide, acetylene
Trichlorethylene	Carbide, acetylene
Chlorohydrin	Fermented alcohol, ethylene
Methanol, formalin	Syngas
Vinyl polymer, acrylic polymer, styrenic polymer, butylene-based polymer, polymerization fiber	Carbide, acetylene Other
Butadiene-based rubber, chloroprene rubber	Carbide, acetylene
Benzene, toluene	Carbide, acetylene
Tanning agent (tannin)	Coal tar

Note: The raw material excepted in law was presumed and determined by the author.
The iso-octane excepted as aviation fuel refers to the Artificial Petroleum Production Industry Law.

Meanwhile, benzene and toluene were expected to start being produced by carbide/acetylene synthesis rather than the conventional method of fractional distillation from coal tar (mainly a byproduct of coke production for iron manufacturing). Tokyo Industrial Research Institute developed this technology in 1938, and Nippon Carbide industrialized 400 tons annual production before the *Organic Synthesis Industry Law* was enacted. However, it was not even able to triple this volume before the end of the war.

Synthesis of aviation fuel isooctane was subject to the *Artificial Petroleum Production Industry Law* rather than the *Organic Synthesis Industry Law*. Domestic production was not achieved by the end of the war, although Chōsen Chisso Hiryō, a Korean subsidiary of Nippon Chisso Hiryō, achieved large-scale production in 1942 at its industrial complex in Hyungnam. By the end of the war, production capacity had reached 45,000 tons of acetaldehyde, 30,000 tons of butanol and 20,000 kL of isooctane. This scale of production was incredibly large for industrial organic chemicals at the time, and was made possible by large-scale hydroelectric power generation, which was not available in mainland Japan. The isooctane was synthesized through an acetylene – acetaldehyde – butanol – evaporation/isomerization/dimerization/hydrogenation process. The process from acetylene to butanol was carried out using Nippon Chisso Hiryō technology, and then the process from butanol to isooctane was carried out using technology developed by the navy fuel factory.

From the enactment of the *Organic Synthesis Industry Law* in 1940 through to 1945, the consumption of carbides was discouraged for fertilizer, and encouraged for organic synthesis, mineshaft lighting, welding and cutting, as shown in Fig. 4.14. Accordingly, while organic synthesis accounted for around 10% of carbide consumption before and after this time period, it rose to around 15% of carbide consumption during this period only. This usage was entirely for the military.

The *Organic Synthesis Industry Law* served as an opportunity to develop large-scale industrial organic chemical and polymer industries in Japan, and provided a platform for launching a large-scale petrochemical industry within a short space of time in the 1950s. These industrial development laws, or business laws, were the starting point for the Japanese government's idea of strong policy intervention in the petrochemical industry from the 1950s to the 1980s.

(3) Synthetic rubber

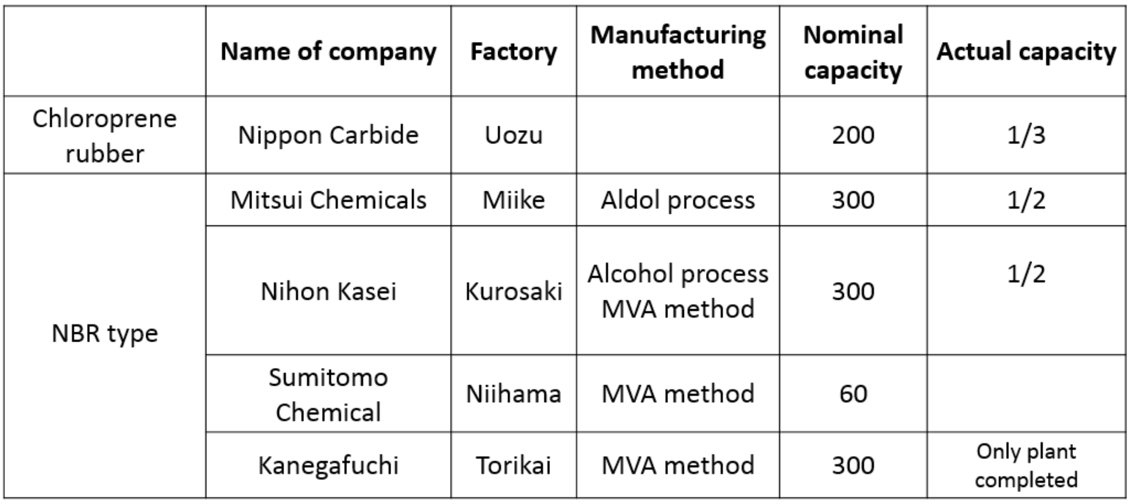
Synthetic rubber was first industrialized during the First World War by German company Bayer, amidst a naval blockade. The rubber produced was methyl rubber polymerized from 2,3-dimethyl-1,3-butadiene. Acetone was synthesized from acetylene, then dimerized by pinacol coupling using metallic magnesium, and then dehydrated to produce dimethylbutadiene, which was then polymerized. While 2,000 tons of synthetic rubber were produced during the First World War, the industry fell into decline after the war, as it could not match the performance of natural rubber. However, a wealth of research was conducted on butadiene manufacturing and polymerization methods after the war, both in Germany and in the United States. Some of this research found that a butadiene-styrene copolymer showed very good performance and could be used in many of the applications for natural rubber. This copolymer was Buna-S, now called styrene-butadiene rubber or SBR. IG Farben was granted the German and American patents in 1929, and constructed a test plant in 1934. Meanwhile, DuPont developed CR by emulsion polymerization of chloroprene, and started industrial production of it in 1932. Although CR never became a substitute for natural rubber, it had a use of its own due to its superior oil resistance. The Standard Oil (New Jersey) developed IIR, an isobutylene-isoprene copolymer, and started industrial production of it in 1943. IIR was used in tire tubes due to its low gas permeability.

During the Second World War, the United States had to focus on developing and producing synthetic rubber as a national policy, as Japan had quickly annexed much of Southeast Asia. The United States produced 2,400 tons of SBR in 1942, 180,000 tons in 1943, 670,000 tons in 1944 and 720,000 tons in 1945. By the end of the war, Germany had an annual production capacity of 150,000 tons and produced 110,000 tons in 1944.

The industrialization of synthetic rubber in Japan was one of the main objectives for enacting the *Organic Synthesis Industry Law*. Table 4.3 shows the companies that produced synthetic rubber in Japan during the Second World War, as well as their production methods and products. The Osaka Industrial Research Institute of the Ministry of Commerce and Industry started researching synthetic rubber in 1935, and established a method of producing butadiene from ethanol by dehydration, dimerizing and dehydrogenating using a magnesium oxide catalyst (the alcohol method). The Institute also perfected a method of extracting butadiene using cuprous chloride, and in 1938 constructed a plant with a 10 kg daily production capacity. The institute also conducted research on polymerization using metallic sodium, as well as copolymerization with acrylonitrile and styrene. In 1939, a number of engineers from the Osaka Industrial Research Institute transferred to Nihon Kasei (now Mitsubishi Chemical), while a butadiene plant with a 1-ton daily production capacity was completed in 1942 under the *Organic Synthesis Industry Law*. Production then started on NBR synthetic rubber.

Table 4.3 Synthetic rubber manufactured in Japan during the Second World War

Production: ton/year



	Name of company	Factory	Manufacturing method	Nominal capacity	Actual capacity
Chloroprene rubber	Nippon Carbide	Uozu		200	1/3
NBR type	Mitsui Chemicals	Miike	Aldol process	300	1/2
	Nihon Kasei	Kurosaki	Alcohol process MVA method	300	1/2
	Sumitomo Chemical	Niihama	MVA method	60	
	Kanegafuchi	Torikai	MVA method	300	Only plant completed

Source: Reference [1]

At the same time, Prof. Junji Furukawa of Kyoto University perfected the technology to produce butadiene by monovinyl acetylene (MVA) reduction. This technology offered a simpler butadiene production process than the alcohol method, and the equipment was also cheaper. Although Nihon Kasei also built an MVA-reduction NBR plant, the war ended without it reaching an adequate production stage due to a shortage of raw materials. Sumitomo Chemical shifted the Kyoto University pilot test facilities to its plant in Niihama, and also separately built an acrylonitrile plant and started producing small quantities of NBR synthetic rubber. Kanegafuchi Industrial Company (now Kaneka) also completed an MVA-method butadiene-NBR plant in early 1945, but the war ended without it having reached sufficient production levels due to air raids and other factors.

Mitsui Mining started its own research in 1937 and perfected a method of producing butadiene via acetaldol by dimerizing acetaldehyde (the aldol process), and also developed NBR synthetic rubber production technology. In 1941, the company started construction of a butadiene plant with a 1-ton daily production capacity under the *Organic Synthesis Industry Law*. It also built an acrylonitrile plant at the same time, and produced NBR synthetic rubber from 1944 until the end of the war.

Nippon Carbide made some advances into chloroprene rubber research, based on studies by Prof. Munio Kotake of Osaka University, and developed a production method using an amino hydrochloric acid catalyst rather than the ammonium chloride used by DuPont. The company completed a plant with a 1-ton daily production capacity in Uozu in 1943, but its actual production was significantly lower than its nominal capacity due to a shortage of raw materials and resources.

Up until the start of the war, the Japanese government and military took the development of a wide range of synthetic rubbers, including SBR, very seriously. However, with Japan annexing the southern regions very soon into the war, it was able to secure a plentiful supply of natural rubber. After that, it only encouraged the development and production of the highly oil resistant NBR and chloroprene synthetic rubbers. From 1943 onwards, once the wartime situation intensified and the supply of natural rubber started becoming problematic, there were not enough resources in the country and it was not possible to build general-purpose synthetic rubber plants no matter how much the government supported it.

(4) Vinyl chloride and PVC

When Japan lost the war in 1945, it lost its munitions demand in one fell swoop. The carbide industry turned its focus to fertilizer once more, as shown in Fig. 4.14. The postwar shortages of food and supplies also meant an increase in the demand for fertilizer, and carbide production volumes revived. Organic synthesis went back to accounting for around 10% of carbide usage. However, acetic acid manufacturers began exploring areas for large-scale demand outside of the conventional areas of acetic acid use (solvents, acetic acid esters, vinegar). One such area of exploration was the industrialization of acetate fiber using acetic anhydride. Another was the development of products from vinyl acetate. Vinyl acetate could be made into vinyl acetate resin, polyvinyl alcohol, and the synthetic fiber vinylon. Production of vinylon started in 1949 by Kurashiki Rayon (now Kuraray), with high hopes for domestically invented and producible synthetic fiber. This was followed by the production of vinylon by Dainippon Spinners (now Unitika), using technology developed by Ichirō Sakurada of Kyoto University. Industrial production of acetate fiber was started in 1955 by Teijin using introduced technology; the following year, Ryoko Acetate also started production under Mitsubishi Rayon.

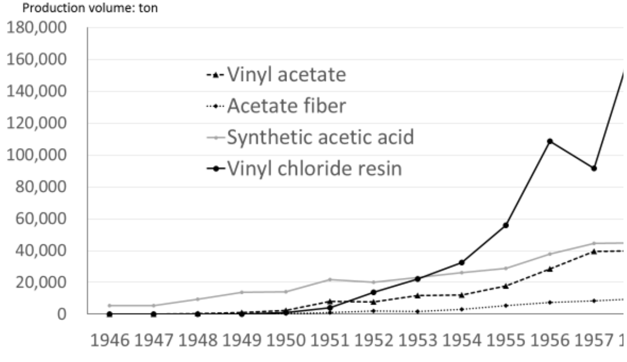
Acetic anhydride and vinyl acetate were linked in their production. The reaction of acetic acid and acetylene co-produces vinyl acetate and ethylidene diacetate, as shown in Fig. 4.15. Over-supply of acetylene at low temperatures raises the vinyl acetate yield, while the opposite yields more ethylidene diacetate. Since pyrolysis of ethylidene diacetate produces acetic anhydride and acetaldehyde, the acetaldehyde can be oxidized and reused as acetic acid.

However, in the 1950s, a large-scale demand emerged that completely differed from the acetaldehyde-acetic acid products that had been the main focus of the acetylene chemical industry since before the Second World War, and within a short space of time, became the mainstay of the acetylene chemical industry. This was vinyl chloride and PVC.

Vinyl chloride is synthesized by reacting acetylene with hydrogen chloride. Emulsion polymerization of vinyl chloride produces PVC. PVC was industrialized in the late 1920s in Germany and the early 1930s in the United States. It appeared in Japan as an imported sample in 1937, and initiatives towards domestic production started right away. In 1941, Nippon Chisso Hiryō industrialized production of PVC (3-ton monthly capacity) at its plant in Minamata, with the idea of exploring new applications for carbides. It also developed its own monomer and polymer production technology. In 1939, it also produced vinyl chloride copolymers. However, the Nippon Chisso Hiryō plant in Minamata was destroyed in an air raid in 1945.

After Japan lost the war, Western technology and market information began to flow into Japan once more. In 1948, Japan imported PVC scraps from the United States, which were distributed out to a dozen manufacturers to research. From 1950 onwards, companies started importing a succession of Western PVC processing equipment. The imported PVC made it possible to create a number of molded products, including wire coatings, film, sheets, leather, belts, tubes and hoses. A number of companies noted these market trends and embarked on domestic PVC production. Nippon Chisso Hiryō, which had been in production during the war, started out in 1949 with a monthly production capacity of 5 ton, followed by a number of other carbide-acetylene manufacturers in 1950 and 1951, including Nihon Kasei (later industrialized in 1951 as Mitsubishi Monsanto Chemical, now Mitsubishi Chemical), Mitsui Chemicals, Kanegafuchi Chemical Industry (now Kaneka), Tekkoosha and Denki Kagaku Kogyo (now Denka). The Yokohama Rubber Company, which had trialed PVC production during the war, established Zeon in 1950, in conjunction with Nippon Light Metal, Furukawa Electric and American company B. F. Goodrich Chemicals. Once Mitsubishi Monsanto Chemical and Zeon started producing PVC using suspension polymerization method, other Japanese PVC manufacturers noted its superior product quality compared to emulsion polymerization, and all started switching over to suspension polymerization method in 1952 and 1953 using introduced technology.

The growth in PVC production volumes was astounding. As Fig. 4.17 shows, it quickly dominated the acetylene chemical industry, overtaking acetic acid, which had been the mainstay of the industry since the acetylene chemical industry began, as well as acetic anhydride/acetate and other acetic acid products with expected postwar growth, and also vinyl acetate and vinylon.



Source: Ministry of International Trade and Industry, chemical industry statistics

Fig. 4.17 Change of production volume of major acetylene products after the Second World War.

(5) Reppe reactions

Industrial development of acetylene chemistry in Japan was mainly through atmospheric pressure reactions, as shown in Fig. 4.18. The main products were acetaldehyde and vinyl acetate synthesis by hydroxy group addition reactions at atmospheric pressure, and trichloroethylene and vinyl chloride synthesis by chlorine or hydrogen chloride addition reactions. Various other acetylene-based industrial organic chemicals were mainly synthesized using acetaldehyde as an intermediate. Acetylene dimerization and pyrolysis reactions rarely attained to product production.

Meanwhile, Walter Reppe of IG Farben in Germany was building up fundamental studies on pressurized acetylene and developed technology to handle it safely, as it carried a risk of explosive decomposition. Reppe went on to discover four major reactions, shown in Fig. 4.19, and systematized acetylene chemistry.

Addition reactions of hydroxy groups and hydrogen halide at atmospheric pressure were generalized as vinylation to produce vinyl compounds, whereby alcohols with active hydrogen, phenol, carboxylic acid, amines, amides and sulfur compounds add to triple bonds under pressure, as shown in Fig. 4.19. Dimerization reactions expanded into trimerized or tetramerized cyclic oligomerization. This is also called cyclic polymerization.

Reactions not found among acetylene reactions at atmospheric pressure include ethynylation and carbonylation, as shown in Fig. 4.19. Ethynylation is a reaction of methine hydrogen (hydrogen immediately adjacent to a carbon-carbon triple bond) in which the carbon triple bonds in the acetylene are preserved. The method of using an ethnylation reaction of acetylene and formaldehyde to produce 1,4-butynediol, then hydrogenating and dehydrating it to obtain butadiene was industrialized in Germany during the Second World War. This was one of the methods of producing butadiene, the raw material for synthetic rubber, in Germany. Carbonylation is a reaction of acetylene, carbon monoxide and substances with active hydrogen, using a carbonyl complex of cobalt, nickel and iron as a catalyst. This produces acrylic acid derivatives.

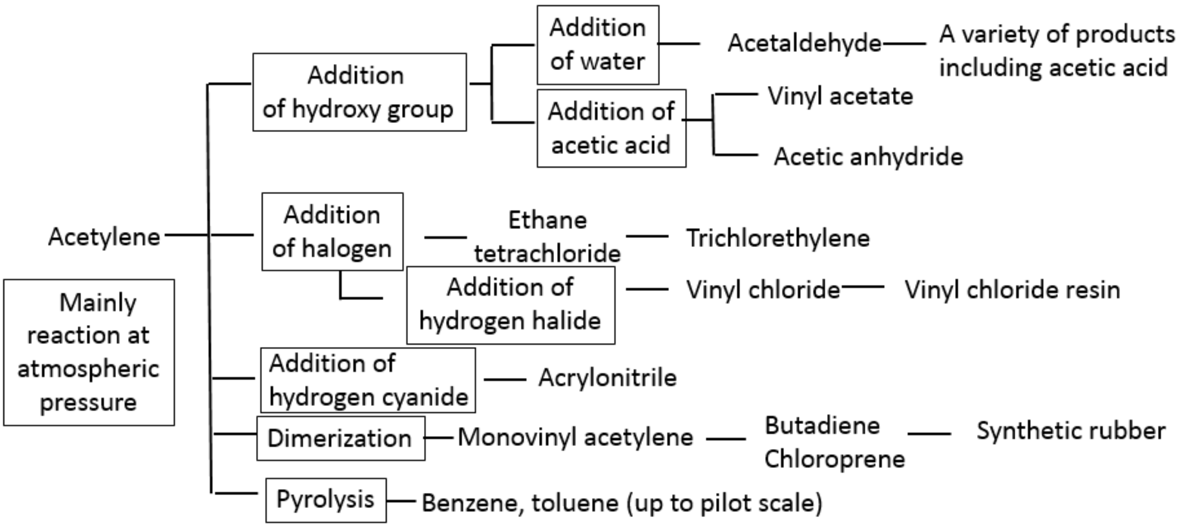


Fig. 4.18 Technology system and major products of acetylene chemistry in Japan before and after the Second World War.

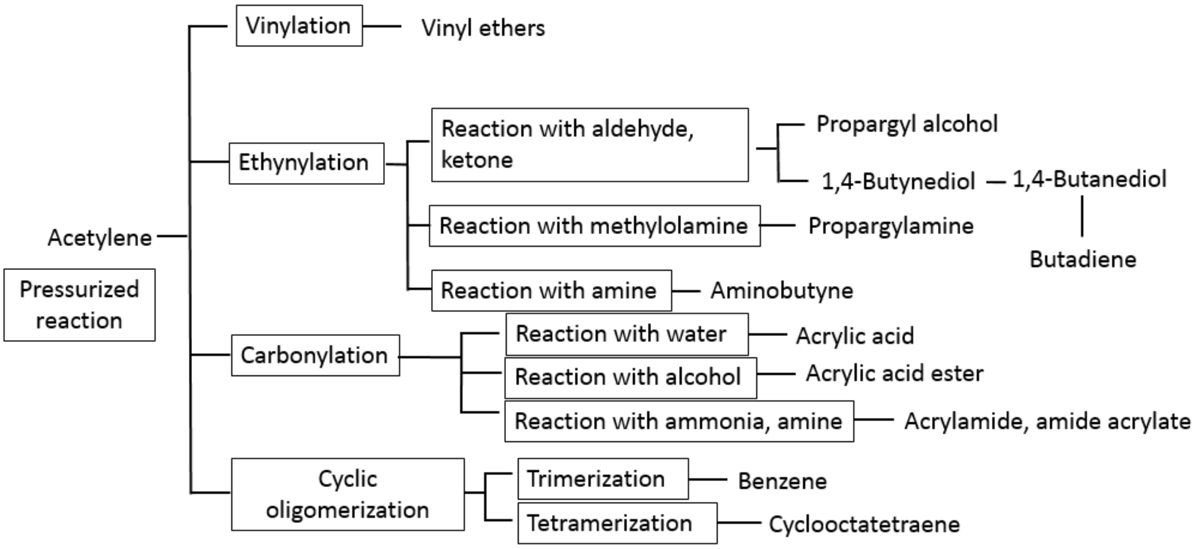


Fig. 4.19 Technology system and major products of Reppe reaction.

Reppe reactions were a type of organic synthesis technology from Germany, which had no petroleum or natural gas resources, only coal. After the Second World War, in the late 1940s, both the academic world and the industrial world in Japan started enthusiastically researching this topic, armed only with the domestic resources of coal and hydroelectric power. When the United States published the PB Report on German wartime science and technology, there was a lot of interest in Reppe reactions. However, once large quantities of petroleum soon began to be imported from the Middle East, and as petrochemistry developed, the move to industrialize Reppe reactions in Japan soon died out, and Reppe reactions were forgotten. Nevertheless, the idea behind the development of Reppe reaction technology continued on in later-developed petrochemical reactions, such as the allyl hydrogen reaction [Footnote 6] and the oxo process [Footnote 7] to produce carbonyl compounds by reacting olefins with carbon

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[Footnote 6] A reaction that preserves the double bonds of the olefin but reacts with the hydrogens in the surrounding methyl groups, producing acrylonitrile, acrylolein/acrylic acid, allyl chloride, maleic anhydride, etc. See Section 6.1.2 (2).

[Footnote 7] A reaction that produces butyraldehyde from propylene, higher aldehydes from α-olefins, and propionaldehyde from ethylene. See Section 6.1.2 (1) 5).

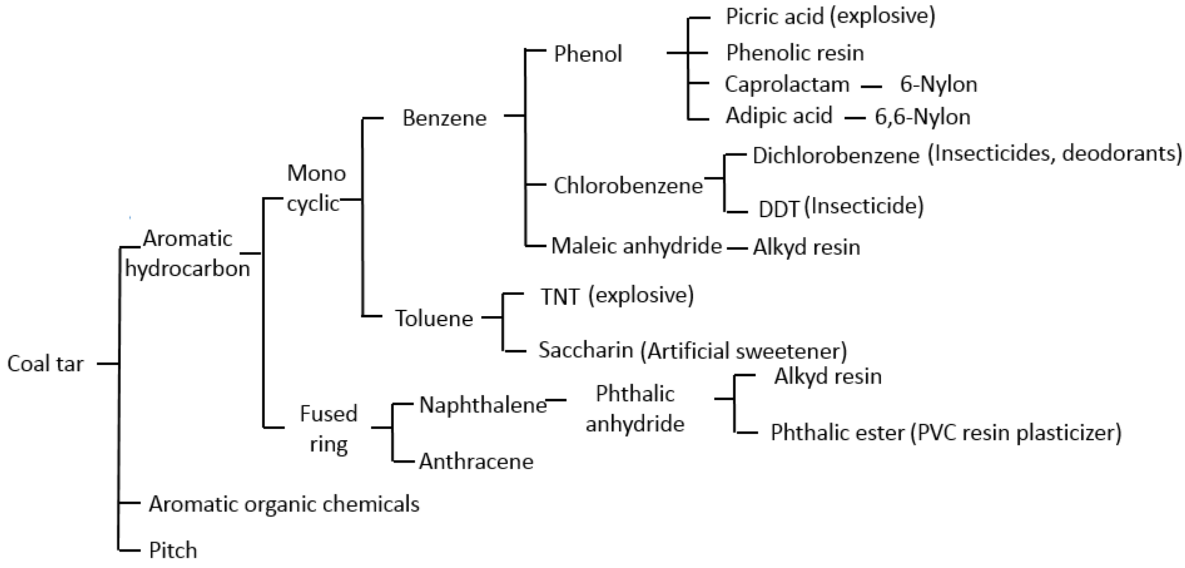
monoxide and hydrogen, although the reaction mechanisms differ from Reppe reactions. It is fair to say that Reppe reactions had a significant impact on later developments in petrochemical technology.

4.6 Industrial organic chemicals and polymers from coal tar

The coal carbonization industry began in the 18th century for producing coke for iron manufacturing, as well as for city gas production (street lighting, fuel, heating). Coal tar was an unwanted byproduct of coal carbonization. Distilling coal tar produced benzene, naphthalene, anthracene and other aromatic hydrocarbons, as well as phenols, cresols, pyridines and other aromatic organic compounds, as shown in Fig. 4.20, with a residue of around 60% (pitch). While aromatic hydrocarbons from petroleum distillation are mainly monocyclic (benzene, toluene, xylene), coal tar also produces a number of fused-ring hydrocarbons (naphthalene, anthracene). For reference, Fig. 4.21 shows the chemical structures of the main aromatic hydrocarbons produced from coal tar, as well as the main industrial organic chemicals produced from them.

The coal-tar-based industrial organic chemical industries were based around the main products produced by distilling coal tar: benzene, toluene, naphthalene and anthracene. The synthetic dye industry started in 1856 by William Henry Perkin, with industries later developing in Germany and Switzerland as well. The synthetic pharmaceutical industry started at the end of the 19th century, as typified by Bayer’s aspirin (acetylsalicylic acid). Perfumes and fragrances and flavorings, artificial sweeteners and a number of other fine chemical industries also began at this time. After the Second World War, coal tar products also came to serve as raw materials for DDT, BHC, 2,4-D, PCP and other pesticides. A very diverse range of aromatic chemical synthesizing technologies developed before the advent of the petrochemical industry. The coal tar chemical industries produced the most diverse range of products and had the most complex structures of all the forests of coal chemistry.

However, many of these low-quantity, high-diversity coal tar chemical industries had no relation to petrochemistry. The mass-produced aromatic industrial organic chemicals that were related to petrochemistry were phenol and phthalic anhydride. Phenol was produced from benzene, while phthalic anhydride was produced from naphthalene, as shown in Fig. 4.20. Other mass-produced aromatic industrial organic chemicals included TDI and MDI from coal tar chemical industries. TDI and MDI were classic coal tar chemistry products: aromatic amines made by nitrating and reducing aromatic hydrocarbons. However, they are omitted in this section as their most significant developments took place in the petrochemical era.



Note: Extremely abundant dye intermediate, pharmaceutical intermediates, perfume intermediates, pesticide intermediates are excluded.

Fig. 4.20 Major product categories of coal tar as raw material.

4.6.1 Phenol

Phenol can be directly obtained from coal tar, and was used in disinfectants and synthetic dyes in the 19th century. The demand for phenol increased significantly in the 1880s when picric acid started being used as an explosive, and the production scale had to shift from that of a dye intermediate to that of an industrial organic chemical. Meanwhile, industrial production of phenol by coal-tar benzene sulfonation process started in Germany in the 1890s. The benzene was sulfonated in concentrated sulfuric acid, then neutralized and melted with sodium hydroxide to produce phenol sodium salt, which was then neutralized to produce phenol. This was a very complicated and labor-intensive method of production. In Japan, Yura Seiko (now Honshu Chemical Industry) industrialized production using its own developed technology in 1915, while the Mitsui Mining Mitsui Dye Plant (now Mitsui Chemicals) did the same using licensed technology in 1916.

With the industrialization of phenol resin in the United States in the 1910s, the demand for phenol grew even more. A chlorobenzene process was industrialized in the United States in the 1920s. This method chlorinated benzene to produce monochlorobenzene, then reacted this with solution of sodium hydroxide in an autoclave to produce phenol sodium salt, which was then neutralized with hydrogen chloride to produce phenol.

The Raschig process was developed and industrialized in the 1930s. This method reacted benzene with hydrogen chloride and air with a copper oxide - iron oxide - alumina catalyst to produce monochlorobenzene, which was then hydrolyzed at the gas phase using a silica catalyst to produce phenol. The byproduct hydrogen chloride was then re-used. The Raschig process was a far more sophisticated method of production.

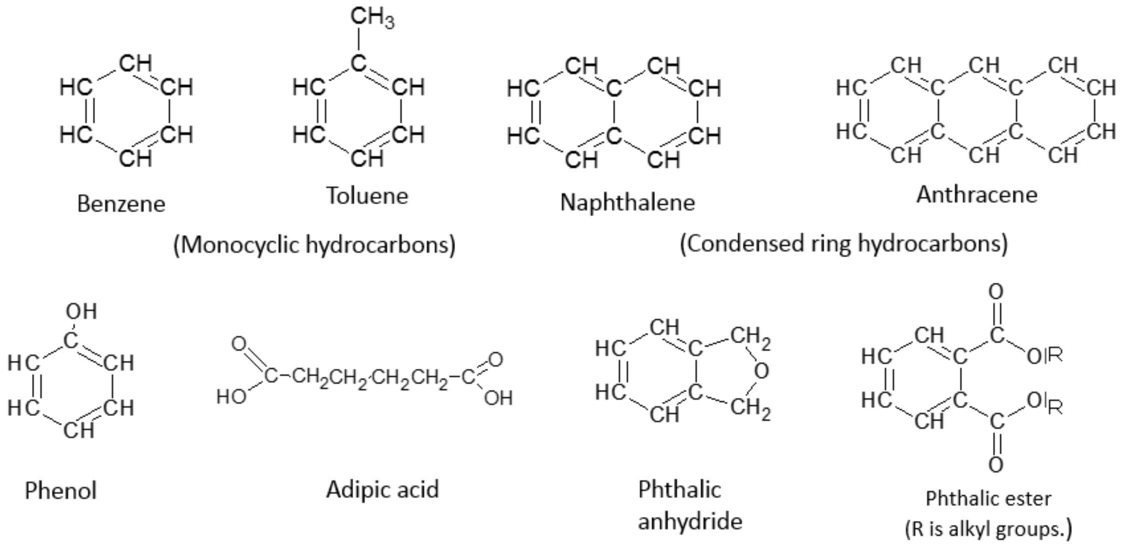
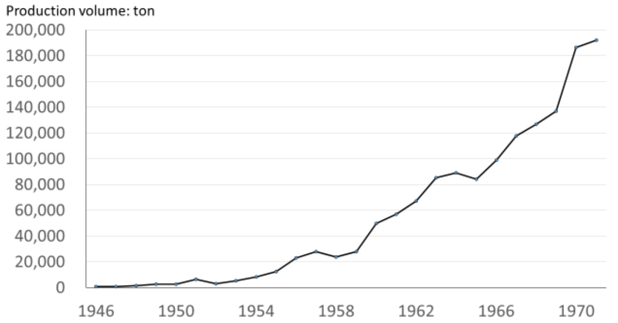


Fig. 4.21 Aromatic hydrocarbons and industrial organic chemicals from coal tar.

In 1939, American company DuPont industrialized 6,6-nylon. The adipic acid used as a raw material for this was made from phenol. DuPont claimed it was “fabricated from such common raw materials as coal, water and air … as strong as steel, as fine as the spider’s web.” German company IG Farben industrialized 6-nylon in the early 1940s, slightly later than DuPont. The raw material for 6-nylon, ε-caprolactam, was also made from phenol. With nylon production increasing rapidly after the Second World War, the demand for phenol also suddenly increased. In Japan, phenol production also rapidly increased from the late 1950s, when industrial production of nylon began in earnest, as shown in Fig. 4.22. Production levels after the war in the early 1950s were on a completely different dimension from prewar levels.



Source: Ministry of International Trade and Industry, chemical industry statistics

Fig. 4.22 Change of production volume of synthetic phenol after the Second World War.

The rapid increase in demand for phenol meant a rapid increase in the demand for benzene as well. However, since coal tar was only produced as a byproduct of coke, it could not support the rapidly-growing demand for benzene.

In 1953, the cumene process, a new phenol production method, was developed in the United States and United Kingdom, and industrialized first in Canada. The cumene process produces cumene from benzene and propylene, which is then oxidized and cleaved to co-produce phenol and acetone. During the Second World War, cumene was produced by petroleum companies as a gasoline-base material for high-octane gasoline. The cumene process was certainly a technology suited to petrochemistry. Right when the petrochemical industry was booming in the West, this method took hold worldwide, ahead of the chlorobenzene and Raschig methods. It was industrialized in Japan in 1959 by Mitsui Petrochemical Industries using introduced technology.

Despite having produced the highest demand for coal-tar benzene, phenol now became completely removed from the coal tar industry, in terms of both supplying raw materials and production technique.

4.6.2 Phthalic anhydride

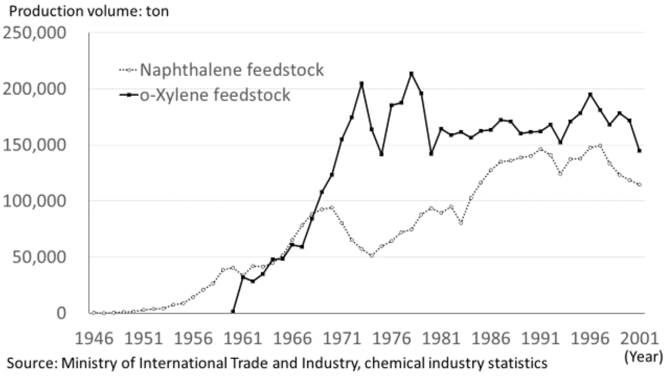
Phthalic anhydride was industrialized in 1896 by BASF as an indigo dye intermediate. It was produced by stoichiometrically oxidizing coal-tar naphthalene using an oxidant such as oleum. An atmospheric oxidation process was developed and industrialized in 1916 using a vanadium pentoxide catalyst. The development of oil-modified alkyd resins in the late 1920s saw an increase in demand for phthalic anhydride. In Japan, synthetic dye companies started producing phthalic anhydride for their own use in the 1930s, while in the 1940s it started being marketed for use in alkyd resins.

In the United States, where o-xylene was readily available from catalytic reformate, the raw material switched from naphthalene to o-xylene in 1945, using the same catalyst. However, in Europe and Japan, the raw material continued to be naphthalene from coal tar.

The rapid increase in PVC production after the Second World War was accompanied by a rapid increase in the demand for phthalic ester as a plasticizer for flexible PVC. In 1952, the first Henkel process, which isomerizes orthophthalic acid made from phthalic anhydride, was developed as a production method for terephthalic acid, a raw material for polyester. In 1958, Kawasaki Kasei Chemicals was the first in the world to industrialize this, followed by Teijin in 1963, resulting in greater increased demand for phthalic anhydride. However, the first Henkel process never became a mainstream method of producing terephthalic acid; even in Japan production had stopped by the early 1970s, and the demand for terephthalic acid did not last long.

In 1960, Nippon Shokubai started producing phthalic anhydride from o-xylene. Later, a number of other companies also transitioned to production using o-xylene, resulting in the rapid popularization of this method in the late 1960s, as shown in Fig. 4.23. Whereas production from coal-tar naphthalene lost two of the naphthalene carbons as carbon dioxide, o-xylene process lost no carbons. Therefore, the naphthalene method was expected to go into rapid decline. However, following the 1970s oil crises, there was a revival of the naphthalene production method, as shown in Fig. 4.23. The naphthalene method continues to compete with the o-xylene method despite its prevalence.

Unlike phenol, coal-tar-based production of phthalic anhydride continued long after the petrochemical method came into being, and continued to compete with it. This is thought to be firstly because the catalyst was almost the same and there was no significant difference in production process costs, unlike phenol, and secondly because there was no demand for naphthalene other than for phthalic anhydride, so it ensured the consumption of products from byproduct coal tar.



Source: Ministry of International Trade and Industry, chemical industry statistics

Fig. 4.23 Change of production volume of phthalic anhydride for each raw material after the Second World War.

4.7 Products and technologies from coke syngas

Syngas is a gas mixture of carbon monoxide and hydrogen. Up until the Second World War, syngas was produced by passing red-hot coke through air and steam. Consequently, the forest of chemical products from syngas came to being as the third of the coal-based forests. When coal is carbonized, it produces large quantities of coke oven gas, which contains carbon monoxide and hydrogen. While the synthetic ammonia industry started in the 1910s using the hydrogen from coke oven gas, coke oven gas was not enough to supply all the ammonia on its own. Therefore, large-scale production of syngas from coke started in the 1910s. This was followed by the large-scale production of syngas in the 1920s as a raw material for methanol synthesis, as shown in Fig. 4.24. Production of artificial petroleum from syngas also started in Germany in the 1930s, using the Fischer-Tropsch process, increasing the production of syngas even further.

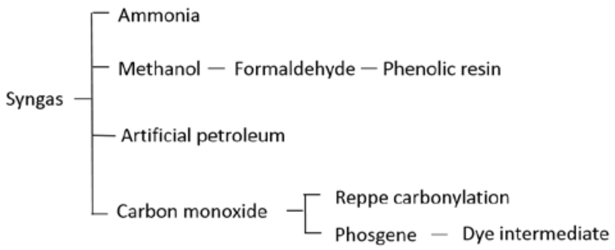


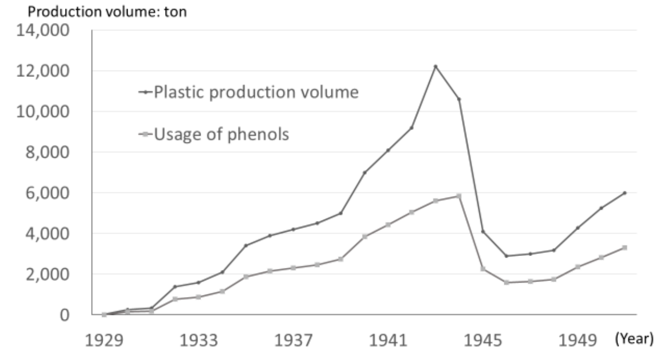
Fig. 4.24 Major products made from syngas before the emergence of petrochemistry.

Another use for syngas is carbon monoxide. Carbon monoxide is used for carbonylation of acetylene with a Reppe reaction. Carbon monoxide also reacts with chlorine to produce phosgene, which is used as a carbonylation agent in the production of dye intermediates and other compounds. Phosgene production and application technology was used after the Second World War to aid the upscaling of isocyanate production as a raw material for polyurethane.

4.7.1 Methanol and formaldehyde

Methanol was extracted from pyroligneous acid in the wood carbonization industry and used as a solvent and chemical raw material. When methanol synthesis from syngas was industrialized in Germany in 1925, wood-carbonization-based methanol suddenly came to an end. Methanol synthesis technology could be said to be an extension of ammonia high-pressure synthesis technology. It was industrialized in Japan in 1932 by Gosei Kogyo (now Mitsui Chemicals) based on research from the Temporary Nitrogen Research Institute (later the Tokyo Industrial Research Institute; now the National Institute of Advanced Science and Technology). This was followed by a number of other companies entering the industry.

The main use for methanol was, and still is, formaldehyde. Formaldehyde was used as a raw material for phenol resin, and was produced by dehydrogenation or oxidative dehydrogenation of methanol. A copper catalyst process originated in Germany in 1889; in 1910, a silver catalyst process was developed as well, with a liquid phase reaction carried out with excessive methanol. In Japan, Edogawa Industrial (now Mitsubishi Gas Chemical Company) started production of formaldehyde in 1926, with a number of other companies later following suit. This was right when phenol resin production was rapidly increasing, as shown in Fig. 4.25. By 1937, there was enough formaldehyde being produced domestically to cover all phenol resin production. The *Organic Synthesis Industry Law* designated methanol and formalin (formaldehyde) as raw materials for phenol resin, aiming to boost production from syngas.



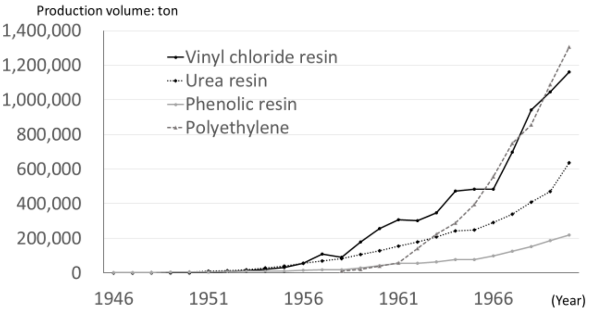
Source: Reference [1]

Fig. 4.25 Change of production volume of plastic and usage of phenols before the Second World War.

While there were essentially no changes in methanol production methods after the Second World War, the raw material for syngas shifted from coke to natural gas. In Japan, Japan Gas Chemical (now Mitsubishi Gas Chemical Company) started producing syngas and methanol from natural gas from Niigata as early as 1952. This was the foundation of the Japanese petrochemical industry, as shall be discussed in Section 5.3.3. In 1958, Toyo Koatsu (now Mitsui Chemicals) started methanol production using natural gas from Mobara, while Akita Petrochemical (a joint venture between Sumitomo Chemical and Teikoku Oil) did the same using natural gas from Akita, followed in 1962 by Nissan Chemical Industries using natural gas from Nagaoka and Kyowa Gas Chemical using natural gas from Nakajo. Petrochemical industries developed all over Japan using this rare domestic resource. Thus, although the production technology for methanol, the core product for syngas chemistry, had been developed in the coal chemistry era, it continued on into the petrochemical era and survived.

While many other raw materials for syngas came along later, such as naphtha, petrochemical waste gas and LPG, ultimately, there was not enough affordable natural gas in Japan, and it came to a sudden end in the 1980s.

An oxidation method of producing formaldehyde using excessive air and an iron oxide or molybdenum oxide catalyst was developed during the Second World War and industrialized by DuPont. Many of the processes in this gas-phase oxidation method were developed after the war by eliminating the reaction heat, and increasing the concentration of formaldehyde produced. Formaldehyde gained new areas of postwar demand for urea resin and melamine resin, along with phenol resin. Urea resin in particular had the highest production volume of all plastics, overtaking phenol resin from the late 1940s to the early 1950s, as shown in Fig. 4.26. It was used in adhesives and electrical components, like phenol resin, and also in tableware, buttons and other everyday molded products, as it did not go brown like phenol resin.



Source: Ministry of International Trade and Industry, chemical industry statistics

Fig. 4.26 Change of production volume of major plastic after the Second World War.

Thus, formaldehyde maintained an important position as a raw material for plastic for around a decade following the Second World War. However, in the late 1950s, urea resin was dispossessed by PVC as the chief among plastics, and furthermore it was outstripped by polyethylene, the mainstay product of petrochemistry, in the early 1960s. Thus, formaldehyde lost its place as a key raw material to acetylene, and then to ethylene.

4.7.2 Artificial petroleum

The *Artificial Petroleum Production Industry Law* was enacted in 1940, aimed at reinforcing artificial petroleum research, industrialization, and increased production in Japan as a matter of national policy. The following four technologies were the main technologies targeted.

(1) Low-temperature coal carbonization
(2) The Bergius process (direct liquefaction of coal)
(3) The Fischer–Tropsch process
(4) Oil shale retorting

Of these, the processes that became the mainstay of production from 1941 to 1945 were (4) followed by (1), as shown in Table 4.4. Oil shale retorting (4) is an old technology that had already been industrialized in the mid-19th century. Since Japan had access to a thick oil shale layer above the Fushun coal mine in Manchuria, it had been exploring uses for it between 1912 and 1926. However, it was not very economical to use European technology, as the Fushun oil shale had a lower oil content than the oil-rich European oil shale, at 6–8%. Manchuria Railway developed an internally-heated retorting furnace, and built a factory in 1929. As the shale oil obtained was heavy, a Dubbs process pyrolysis furnace was promptly brought in from the United States, and production started in 1935.

Table 4.4 Production volume of artificial petroleum in Japan and Manchuria during the Second World War

Unit: Kl

	Year 1941	Year 1942	Year 1943	Year 1944	Year 1945
Low-temperature coal carbonization	49,180	65,141	90,473	95,420	25,153
Bergius process	0	770	0	692	0
Fischer-Tropsch process	7,695	11,243	15,397	16,022	3,986
Oil-shale retorting	137,776	163,282	160,141	83,145	16,526
Total	194,651	240,436	266,011	195,279	45,665

Source: Reference [1]

The technology for (1) low-temperature coal carbonization was also very old technology, originating in 18th-century Germany. In Japan, Osaka Kanryu Kogyo started production using this technology in

1922. During the Second World War, eight large-scale plants were established: Chōsen Chisso Hiryō in Hamgyong (1932), Japan Iron & Steel in Muroran, Ube Nitrogen Industry in Ube, Mitsubishi Mining in Naihoro, Tokyo Gas in Tsurumi, Nissan Chemical in Wakamatsu, Ube Yuka in Ube and Sakhalin Artificial Petroleum in Naibuchi. While six of the plants used non-caking coal as a raw material and were able to use introduced technology from Germany, the Japan Iron & Steel plant in Muroran and the Tokyo Gas plant in Tsurumi used caking coal as a raw material and so had to use their own technology.

By contrast, technology for (2) the Bergius process (direct liquefaction of coal) and (3) the Fischer–Tropsch process was developed early in the 20th century in Germany. The Bergius process (2) was developed in the 1910s by Friedrich Bergius. In this process, coal powder was added to heavy oil and then liquefied by high-pressure hydrogenation. IG Farben acquired the patent from Bergius in 1927 and carried out further research and improvements. A low level sulfur poisoned catalyst was developed, and industrial production started in 1932 using lignite as a raw material. The resulting product was high in aromatic hydrocarbons and served as the artificial petroleum most suitable for aviation fuel. Since IG Farben kept the technology a secret, in Japan, the navy fuel factory carried out its own independent research. In 1935, the navy commissioned the construction of plants in Fushun by Manchuria Railway and Aoji by Chōsen Chisso Hiryō. However, these never reached sufficient production levels by the end of the war as the technology was incomplete, as shown in Table 4.4. Meanwhile, the Fischer–Tropsch process (3) used a cobalt catalyst to synthesize liquid hydrocarbons from syngas at pressure levels from 1–10 atm. Since the resulting product was a straight-chain hydrocarbon, it had the disadvantage of a low octane number. It also had a wide carbon number distribution and would not always produce adequate quantities in the necessary gasoline fraction. Nevertheless, when the German patent was disclosed in 1925, researchers all around the world started working on how to improve it. In Japan, this was done at the Genitsu Kita Laboratory at Kyoto University, and later developed independently using an iron catalyst.

In Germany, the process was industrialized in 1936 by Ruhrchemie, with a number of other companies following suit. As a result, Germany had a production capacity of 740,000 tons during the Second World War, with production levels reaching as high as 570,000 tons. In Japan, Mitsui Mining signed a technology licensing agreement as early as 1936, constructing a plant in Omuta and starting operation in 1940. While the company underwent a variety of changes during the war, the majority of product made using the Fischer–Tropsch process was produced at this factory in Omuta, as shown in Table 4.4.

In 1937, the government enacted the *Imperial Fuel Industry Company Act*, and established a special company for the purpose of producing artificial petroleum. Plants using a 10 atm increased pressure method were constructed in Takigawa (Hokkaido Artificial Petroleum) and Amagasaki (Amagasaki Artificial Petroleum), and the Takigawa plant started production in 1943. In 1944, the Omuta, Takigawa and Amagasaki artificial petroleum companies merged to form the Nippon Artificial Petroleum Company, with the aim of boosting artificial petroleum production through technology exchange, utilizing materials and facilities, dedicating Omuta to catalyst production and other initiatives. However, although the Fischer–Tropsch process was where the government spent most of its efforts, artificial petroleum production using this method also remained low at the end of the war, as shown in Table 4.4.

The artificial petroleum division at Omuta branched out on its own as Miike Gosei Chemical Industry in 1946, using the artificial petroleum plant coke ovens and syngas facilities to supply syngas to neighboring Toyo Koatsu as a raw material for ammonium sulfate. The company later put the rest of the unused artificial petroleum facilities to use and started producing petroleum-based synthetic detergent.

Of all the Mitsui chemical companies, Miike Gosei Chemical Industry is notable as the first postwar petrochemical industry and for having played a pioneering role in domestic petrochemical production. The company's experience with artificial petroleum technology arguably gave it the insight to see the potential in the petrochemical technology developed in the United States. However, in the late 1950s, as the raw material for ammonia gas started changing in earnest from coke and coal gasification to petroleum gasification, natural gas and petrochemical waste gas, Miike Gosei could no longer support its coke oven operations. Thus, all operations using inherited artificial petroleum facilities came to an end.

There are various opinions on the role played by artificial petroleum technology in the formation of petrochemical technology. IG Farben, which had worked on the direct liquefaction of coal, (2) above, collaborated with the Standard Oil (NJ) and other companies in the early 1930s by providing hydrogenation patent rights. Since this contributed to the development of heavy oil hydrocracking technology and other American technologies, there is an idea that this formed the basis for the creation of petrochemical technology. However, heavy oil pyrolysis technology developed in the United States in the 1910s, and ethane steam cracking technology in the early 1920s, before artificial petroleum technology was developed. Accordingly, it is difficult to give credence to the idea that artificial petroleum technology gave rise to petrochemical technology. In terms of mastering large-scale, continuous operation technology, methanol and artificial petroleum can be viewed as having laid the foundation for the ready adoption in the 1950s of American petrochemical technology in areas like Europe and Japan, where no large-scale petroleum refining technology had developed.

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5 History of the petrochemical industry

As mentioned at the beginning of the previous chapter, petrochemistry began as a small forest in the United States in the 1920s, existing alongside and competing with forests from other more prevalent materials for 30 years. The field as we know it today did not exist in Europe and Japan; however, it began making inroads into Europe in the 1950s and changed dramatically with the incorporation of European chemical technology. Crude oil was discovered in the Middle East in the 1930s, but major exports did not begin until the 1950s, after which time it became a cheaper source of energy than coal and products derived from fermentation. This is another major reason for the change in the petrochemical industry.

The 1960s proved to be a period of *Sturm und Drang* for petrochemistry. Researchers in the field were developing a rapid succession of technologies that could enable the cheaper production of products typically yielded through other chemical processes. Thus, petrochemistry soon overtook other fields engaged in the mass production of chemical products to assume sole possession of the chemical industry. From the 1970s onward, several crises, from environmental and energy issues to chemical pollution and global warming, have threatened to unseat petrochemistry. This has led to a partial revival of the fields of oleochemistry and fermentation chemistry, with some countries, such as China, trying to put policy measures in place to restore coal chemistry for the sake of economic security. For over 50 years, however, the field of petrochemistry has successfully maintained its position at the foundation of the chemical industry by offering solutions to various problems that have arisen.

From its origins in the developed nations, petrochemistry began to spread to every corner of the world in the 1970s. Consequently, regions rich in raw materials of oil and natural gas came to develop a strong competitive edge in the field of petrochemistry. In many cases, this shift was politically motivated, such as Saudi oil prices, and fraught with many issues. Since letting the chemical industry deteriorate was not an option, regions that were not blessed with these resources went through a process of trial and error to keep petrochemistry alive. From this came initiatives in functional chemistry that stretched beyond the conventional scope of the field of petrochemistry as well as the development of new technologies with the potential to transform petrochemistry from its roots.

5.1 The 1920s: An industry is born in the United States

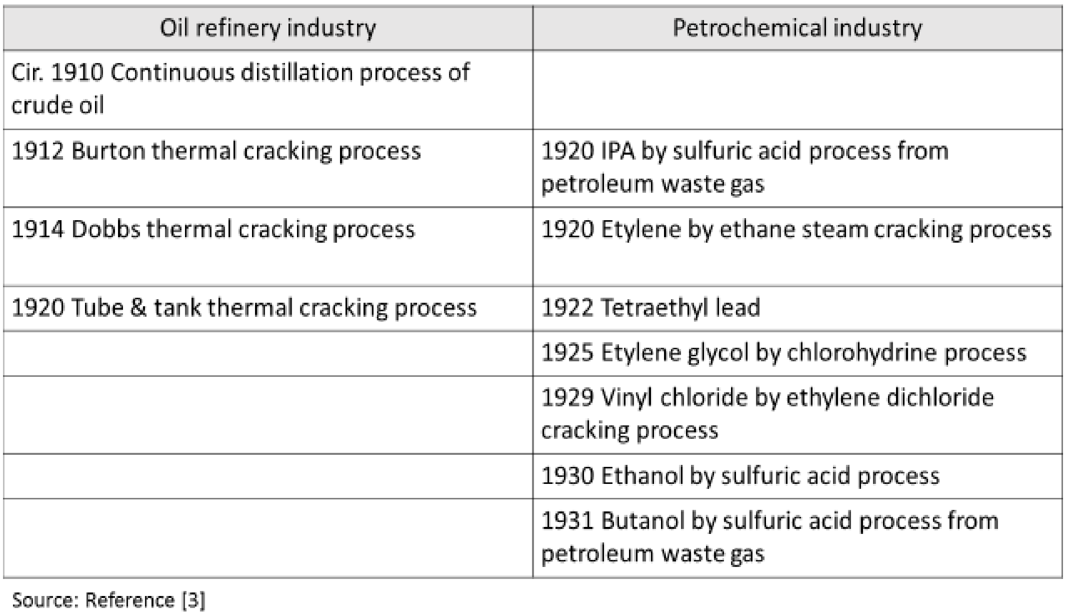
The oil industry in the United States began with the successful drilling of an oil well in Pennsylvania by Edwin Drake in 1859. By the end of the 19th century, a raft of new oil fields had sprung up across the United States, in states such as Illinois, Kansas, Oklahoma, Texas, Louisiana and California. Initially, kerosene was the primary driver of the demand for oil; however, when the Model T Ford went on sale in 1908 and ushered in an era in which the automobile became accessible to everyone, the demand for oil in the United States shifted to gasoline, which remains the case to the current day.

It was in this context that oil refining technologies were developed, as shown in Table 5.1, and from this grew the petrochemical industry.

5.1.1 Thermal cracking of heavy oil

The oil refining system for continuous distillation was introduced in 1910. Gasoline accounted for a large portion of the oil demand in the United States, but the distillation of crude oil resulted in an excess of heavy oil. Therefore, to increase the gasoline yield from crude oil, refineries began to thermally crack oil, and in particular, heavy oil. The Burton process was developed in 1912, followed by the Dubbs process in 1914, and multiple other thermal cracking processes were developed thereafter. Thermally cracked heavy oil yields gasoline and other light distillates, as well as petroleum waste gas containing hydrogen, alkanes and lower olefins (i.e. ethylene, propylene and butylene) and large amounts of carbon.

Table 5.1 Oil refinery and petrochemical industry in the U.S. in the 1920s to the early 1930s (excluding organic chemicals or polymers made from raw materials other than natural gas or oil)



Oil refinery industry	Petrochemical industry
Cir. 1910 Continuous distillation process of crude oil	
1912 Burton thermal cracking process	1920 IPA by sulfuric acid process from petroleum waste gas
1914 Dobbs thermal cracking process	1920 Etylene by ethane steam cracking process
1920 Tube & tank thermal cracking process	1922 Tetraethyl lead
	1925 Etylene glycol by chlorohydrine process
	1929 Vinyl chloride by ethylene dichloride cracking process
	1930 Ethanol by sulfuric acid process
	1931 Butanol by sulfuric acid process from petroleum waste gas

Source: Reference [3]

5.1.2. The birth of the petrochemical industry

In 1920, chemists at Standard Oil (NJ) Bayway Refinery caused a reaction between the propylene from petroleum waste gas and sulfuric acid to create propyl sulfate, which they then combined with water to produce Isopropyl alcohol (IPA). This is considered to be the beginning of the petrochemical industry. Isopropyl alcohol was oxidized to give acetone, and also used as a solvent. Using a similar technology, Shell altered the concentration of the sulfuric acid in butylene, yet another substance in waste gas, to successfully separate out n-butylene and isobutylene. In 1931, the company went on to produce sec-butyl alcohol and MEK from n-butylene. MEK, like acetone, was also used as a solvent.

5.1.3 Steam cracking of ethane

Meanwhile in 1920, Union Carbide and Carbon founded a subsidiary called Carbide and Carbon Chemicals which began producing ethylene in its Clendenin, West Virginia facility by the steam cracking of ethane separated out from natural gas. Unlike the old process that entailed the thermal cracking of heavy oil at a high temperature under high pressure, this innovative method reduced partial pressure and shortened retention time with the addition of steam. Thus was born the method for steam cracking oil and natural gas, which remains to this day an important technique for the production of basic petrochemicals. The technique used to separate ethane from natural gas and ethylene from product gas was low-temperature distillation. Linde Air Products, one of the four companies involved in the establishment of Union Carbide and Carbon, contributed significantly to the development of this technology in 1917. Linde AG, the German parent company of Linde Air Products initially achieved the successful industrial application of air liquefaction equipment and equipment that used the distillation of liquid air for separation from around the end of the 19th century to the turn of the 20th century (see Section 2.3.2).

5.1.4 Development of ethylene products

In 1925, Union Carbide and Carbon reacted ethylene and chlorine with water to create ethylene chlorohydrin, which it then hydrolyzed to produce EG. At that time, EG was solely used as automotive antifreeze, and the company held a monopoly over the substance up until the Second World War broke out. By developing a use for ethylene dichloride (EDC), a byproduct from the production of ethylene chlorohydrin, the company also pioneered the market for dry cleaning solvents. In 1929, the company began producing polyvinyl chloride (monomer), which was created from the thermal cracking of EDC. Around this time in Germany, a polyvinyl chloride was developed, although polyvinyl chloride had been recognized as a compound since the 19th century. Union Carbide and Carbon had also attempted to polymerize this compound, but failed for the lack of the photostabilization and molding technologies required to produce polyvinyl chloride. Not long after this, however, the company succeeded in developing a special polyvinyl chloride by copolymerizing polyvinyl chloride and vinyl acetate; this polyvinyl chloride started being used by the vinyl record industry in the United States.

In 1926, Union Carbide and Carbon synthesized ethylene oxide by dehydrochlorinizing ethylene chlorohydrin in an alkaline solution. As mentioned in Section 3.4.2 (2), ethylene oxide is a highly reactive organic intermediate that now has myriad applications. At that time, however, it was reacted with cellulose to produce Cellosolve, an ingredient in lacquer solvent. In 1931, the French chemist T.E. LeFort invented a method for creating ethylene oxide by the direct oxidation of ethylene using a silver catalyst. Union Carbide and Carbon adopted this method, and launched the first industrial application of this method in 1937. After this, it was found that EG could be produced by reacting ethylene oxide with water, thereby eliminating the need to first produce ethylene chlorohydrin. In the early days of the petrochemical industry, the invention of methods like LeFort’s, which permitted the direct oxidation of olefins with a solid catalyst, was astonishing.

In 1930, Union Carbide and Carbon began producing ethanol from ethylene by applying the sulfuric acid process to ethylene. This was the same technique that Standard Oil (NJ) used to produce IPA and Shell used to produce sec-butyl alcohol, as mentioned previously. Around this time, Union Carbide and Carbon also began producing acetaldehyde by oxidizing ethanol. Coinciding with this, the company ceased producing acetylene-based acetaldehyde at its Niagara Falls plant.

In 1922, Standard Oil (NJ) began commercially manufacturing tetraethyl lead, a gasoline octane enhancer discovered by GM the year before at its Bayway refinery. The ethyl chloride used in this process was derived from ethylene contained in the waste gas produced during the thermal cracking of heavy oil. There was more ethylene in the waste gases produced during thermal cracking than in the catalytic cracking of heavy oil, a process that was developed later and adopted widely. In 1923, DuPont also opened a factory to produce tetraethyl lead. DuPont used fermentation ethanol to produce ethyl chloride. GM and Standard Oil joined forces to establish a tetraethyl lead manufacturer called Ethyl, thus putting the production of the compound into high gear. To supply Ethyl with the ethylene it needed, Standard Oil built a propane steam cracking facility to replace the old practice of collecting ethylene from heavy oil pyrolysis waste gas. This technology was based on the ethane steam cracking process used by Union Carbide and Carbon, but using propane yielded more products, so new separation and collection technologies were needed. The company also pursued research into the steam cracking of naphtha and gas oil, as will be discussed in the next section.

Thus, the petrochemical industry gradually grew in step with the expansion of the oil refining industry during the 1920s and the 1930s. Notwithstanding, the demand for compounds other than tetraethyl lead was limited to solvents and antifreeze agents such as oxygen-containing alcohols and ketones. At this point, no connection had been made with polymers, and the industry remained small. The biggest oxygen-containing compound of this era was still fermentation ethanol. Therefore, even though it is true that the petrochemical industry originated in the United States, its scale remained limited.

5.1.5 Wood chemistry and coal chemistry usher in the polymer era

The United States of the 1920s was the

world's first mass consumer society. In 1930, the first supermarket was opened. Concurrent with this, the use of plastic began to spread throughout the United States from the 1920s onwards, ushering in the dawn of an era of polymer materials. These polymers, however, were not derived from oil, but from wood and coal. The polymers that were frequently used in the United States in the 1920s included celluloid, phenolic resin, viscose rayon and acetate. By the 1930s, these were joined by moisture-proof cellophane, urea resin, polyvinyl acetate, polyvinyl chloride, methacrylate resin and chloroprene rubber. Nylon was developed at the end of the 1930s, leaving a lasting impression on people the world over, and marking the dawn of the polymer era, not only for the United States, but for the rest of the world as well.

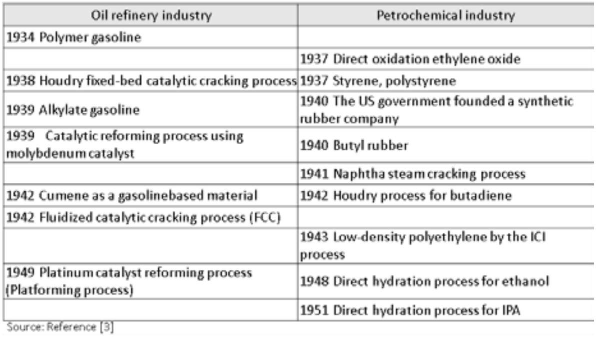
Other than the United States, many of the countries that developed these polymers were in Europe. Consumerism had yet to take root there at that time. Plastic was seen as a cheap substitute for other materials, and its benefits, such as the freedom it allowed in product design, were not as highly regarded as they were in the United States. Accordingly, the polymer age had not yet begun in Europe.

In Japan, meanwhile, the industrial production of celluloid and viscose rayon had begun in the early 20th century and started booming in the 1920s. By 1937, Japan had become the world's biggest producer of both of these polymers (see Section 4.1). This, however, was merely in response to export demand from the United States; Japan had not yet experienced the full effects of consumer society. The production of synthetic compound phenol resin began in the 1910s, and the use of electric lamps, radio parts and other electrical components, rayon manufacturing pots and spinning machinery components started spreading in the 1930s, , although Japan was still a far cry from the dawning of the polymer era.

5.2 The 1940s: Advances in the American petrochemical industry

After roughly 20 years, the petrochemical industry in the United States transitioned out of infancy with a major boom in the Second World War, with the mass production of synthetic rubber as the catalyst. An outline of the advancements in oil refining and petrochemical technologies in the latter half of the 1930s can be found in Table 5.2.

Table 5.2 Oil refinery and petrochemical industry in the U.S. in the late 1930s to the 1940s
(excluding organic chemicals or polymers made from raw materials other than natural gas or oil)



Oil refinery industry	Petrochemical industry
1934 Polymer gasoline	
	1937 Direct oxidation ethylene oxide
1938 Houdry fixed-bed catalytic cracking process	1937 Styrene, polystyrene
1939 Alkylate gasoline	1940 The US government founded a synthetic rubber company
1939 Catalytic reforming process using molybdenum catalyst	1940 Butyl rubber
	1941 Naphtha steam cracking process
1942 Cumene as a gasolinebased material	1942 Houdry process for butadiene
1942 Fluidized catalytic cracking process (FCC)	
	1943 Low-density polyethylene by the ICI process
1949 Platinum catalyst reforming process (Platforming process)	1948 Direct hydration process for ethanol
	1951 Direct hydration process for IPA

Source: Reference [3]

5.2.1 Catalytic cracking of heavy oil

In 1938, French engineer Eugene Houdry developed the fixed-bed catalytic cracking process as a replacement for the thermal cracking of heavy oil, with the aim of increasing gasoline yield. Once this technology was adopted in the United States, it spread like wildfire. Fluidized catalytic cracking (FCC), the process currently used around the world today, was developed by Standard Oil (NJ) and was adopted at their Baton Rouge refinery in 1942. However, FCC was not widely adopted in the United States or anywhere else in the world until after the war. Since catalytic cracking employed a different reaction mechanism from thermal cracking, it generated much more petroleum waste gas. This, however, had a different composition from the petroleum waste gas generated by thermal cracking; it contained very little ethylene and large amounts of propylene and butylene. With the widespread adoption of catalytic cracking, the supply of lower olefins began to skyrocket in the United States in the early 1940s. Thus began the fully-fledged development of olefin chemistry.

5.2.2 Mass production of gasoline-based materials from petroleum waste gas

As mentioned previously, alcohol is produced by causing a reaction between an olefin and sulfuric acid. By changing the reaction conditions and using hot sulfuric acid, butylene undergoes acid-catalyzed dimerization to generate polymer gasoline [Footnote 1]. This polymer gasoline can then be hydrogenated to obtain isooctane. Isooctane was a key ingredient in aviation fuel, which has to have a high octane number. Shell opened an isooctane plant in 1934, and Standard Oil (NJ) soon followed suit.

In 1939, both companies succeeded in commercially producing alkylate gasoline through the alkylation of isobutane with butylene and propylene. As opposed to polymer gasoline, alkylate gasoline does not need to undergo hydrogenation after dimerization. In 1942, Shell successfully used an acid catalyst to synthesize cumene from benzene in coal tar and propylene in petroleum waste gas. Cumene, polymer gasoline, isooctane and alkylate gasoline all have high octane numbers and were used as key ingredients in good quality gasoline-based materials. In particular, they were in high demand as essential aviation fuels during the Second World War. While these gasolines were mass produced using olefin chemistry, it was the petroleum refining industry that created and used them, rather than the chemical industry.

Also in 1939, German company IG Farben developed a process for the catalytic reforming of naphtha (using a molybdenum oxide-alumina catalyst). During the war, this technology was applied by Standard Oil (NJ), Standard Oil (Indiana), and the Kellogg Company, which helped boost the supply of high-octane gasoline. However, since a sufficient supply of aromatic hydrocarbons to the chemical industry in the United States could be obtained from the distillation of coal tar, it was exclusively obtained this way during the Second World War, other than some obtained from toluene [Footnote2][1]..

5.2.3 Steam cracking of naphtha

As mentioned previously, Standard Oil (NJ) successfully developed a method for the steam cracking of naphtha, which it put into commercial use in its Baton Rouge refinery in 1941. Unlike the processes based on ethane and propane, the use of naphtha enabled the production of butadiene, an important compound for the United States during the Second World War, as outlined below. In order to obtain butadiene from a C4 fraction from the steam cracking of naphtha, Standard Oil (NJ) first developed an extraction method using a copper ammonia solution.

5.2.4 Synthetic rubber production increases

During the Second World War, the United States government put the Synthetic Rubber Program into action, which was a plan to build factories to boost the production of synthetic rubber. This served as the largest trigger for the advancement of the American petrochemical industry. As the Japanese army had captured the Malay Peninsula and Indonesia early in the war, it became clear to the United States that it would soon suffer a shortage of natural rubber. Accordingly, the government devised a plan to dramatically increase the production of synthetic rubber. The United States needed a particularly large amount of SBR, which was used to make tires (see Section 4.5.2 (3)). It also needed the highly oil-resistant NBR. These synthesizing technologies were part of IG Farben’s synthetic rubber research conducted under an expanded technology alliance agreement concluded between IG Farben and Standard Oil (NJ) in 1930; thus, it was through Standard Oil (NJ) that the government became aware of these technologies. Accordingly, the government was able to execute its Synthetic Rubber Program within an extremely short time frame. By contrast, as mentioned in the previous chapter, Japan was much further behind in its efforts to commercialize synthetic rubber.

5.2.5 Butadiene

There were several avenues for the supply of butadiene, the primary raw material in synthetic rubber. In 1943, Humble Oil, a subsidiary of Standard Oil (NJ), built a

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[Footnote 1] Polymer gasoline is an imprecise term used in the petroleum refining industry. It is an established term, although as a hydrocarbon with around C8, it is not a true polymer.

[Footnote 2] The demand for toluene during the war focused heavily on its use as a raw material for explosives.

butylene dehydrogenation plant. When the supply of butylene from petroleum waste gas grew short, it then developed a method to dehydrogenate butane (i.e. the Houdry process). This technology was abandoned after the Second World War due to its high cost. In addition, the company also used the aforementioned process developed by Standard Oil (NJ) to extract butadiene from a C4 fraction from the steam cracking of naphtha. Surprisingly, however, the greatest source of butadiene was fermentation ethanol. In the United States, fermentation ethanol was made from corn. Due to the influence of the agricultural lobby, the mainstream process was a long one: acetaldehyde and aldol were condensed from fermentation ethanol, then hydrogenated and dehydrated. During the war, Union Carbide significantly shortened the process with the development of a new method for producing butadiene by condensing ethanol and acetaldehyde using a silica catalyst. Union Carbide mass produced synthetic ethanol from the ethylene obtained by the steam cracking of ethane and used this as the raw ingredient for butadiene.

5.2.6 Linking olefin chemistry and polymers

Styrene, the other main ingredient in SBR synthetic rubber, was first put into production by German company IG Farben in 1930 in the form of polystyrene. In the United States, Dow Chemical began producing polystyrene in 1937, but the scale of the operation was so small that almost no one in the market knew about it. However, during the Second World War, styrene became an indispensable raw material for SBR tires, so efforts to step up production were undertaken by four companies: Dow Chemical, Monsanto, Koppers, and Union Carbide. The benzene for synthetic rubber was obtained entirely from coal tar. During the war, styrene demand was essentially driven by SBR alone. Meanwhile, polystyrene production volume remained small, as it was primarily only used by the military as an insulating material for radars. Another essential material used in radar insulation was low-density polyethylene (LDPE), invented by British company ICI in 1933 and put into production in 1939. In The United Kingdom, fermentation ethanol was the raw material used to make ethylene. During the Second World War, ICI provided its technology to the United States, and in 1943, both Union Carbide and DuPont opened ethylene factories.

Meanwhile, Standard Oil (NJ) developed and commercialized butyl rubber, which has an excellent gas barrier, making it ideal for use in tire tubes. This was a special rubber produced by the polymerization of isobutylene and a small amount of butadiene at low temperatures. After the war, isoprene obtained from the steam cracking of naphtha was used in place of butadiene.

In this way, the United States petrochemical industry, which had been unable to create any lasting linkages with polymers up through the 1930s, finally started doing so during the Second World War with polymers such as synthetic rubber, polyethylene and polystyrene. Meanwhile, private-sector demand shrank during the Second World War for celluloid, phenol resin, urea resin, polyvinyl chloride, methacrylate resin and nylon, which had already ushered in the polymer age in the United States in the 1920s and 1930s, while demand coming almost exclusively from the military led to stepped up production. For example, the nylon fibers that first went on sale in the form of stockings were used during the war for parachutes, tents and ropes as well as a variety of other wartime goods, such as mosquito nets used to protect soldiers in the tropics. Polyvinyl chloride, used to make soft vinyl chloride products, was also important as a flame-retardant wire coating material. However, these plastics and synthetic fibers that were mass produced in the United States during the war were still mostly derived from wood and coal.

5.2.7 Interest in polymers increases

The United States army brought with it American-made plastic and synthetic fiber products to the European front, resulting in the superiority of these products coming to be recognized in Europe as well. Meanwhile, in Germany, which had also ramped up its synthetic rubber production during the war like the United States had, demand for butadiene increased rapidly. The demand for the antifreeze EG and ethylene, the source of the styrene used in synthetic rubber, also skyrocketed. In Germany, the primary raw material for these chemical products was coal (from acetylene, coke oven gas and coal tar), but fermentation ethanol was also an important raw material.

Products that were manufactured in the United States as important military goods were also known in Japan, such as polyvinyl chloride, polyethylene, polystyrene, synthetic rubber and nylon fiber. Japan scrambled to ramp up its domestic production of these goods, and, as mentioned in the previous chapter, research was undertaken, backed by the government and the military. The raw materials for these products were domestically-available coal and fermentation ethanol. Research and development progressed despite the lack of information from the West, and, during the war, Japan managed to put several polymers into production, although production volumes were minimal. 1940s Japan had yet to see the dawning of the age of synthetic polymers that would replace the cellulose-based polymers of the 1930s.

5.3 The 1950s: The fusion of American petrochemical technologies and European chemical technologies

By the 1950s, the petrochemical industry was no longer confined to the United States; it had spread to Europe and Japan. The integration of petrochemical technologies with manufacturing technologies for the mass production of chemical products, which had made advances in Europe even before petrochemistry began, kick-started a massive expansion of those products and technologies.

Since Europe and Japan did not produce their own ethane-containing natural gas, the primary method for obtaining basic petrochemicals was the steam cracking of naphtha and other light petroleum products. The steam cracking of naphtha and other substances yielded a variety of olefins and cracked gasoline. Cracked gasoline became the main source of aromatic hydrocarbons due to the large amount and high concentration of these compounds it contains. Meanwhile, in the United States, a method was developed to extract and recover aromatic hydrocarbons from catalytically reformed naphtha, mass produced in an effort to obtain high-octane gasoline, and it was soon adopted widely. This technology was also used to recover aromatic hydrocarbons from cracked gasoline. Throughout the 1950s, the source of aromatic hydrocarbons in both the United States and in Europe shifted significantly from coal tar to petroleum. The same shift began in Japan in the late 1950s, about five years behind Europe.

In the field of industrial organic chemical production technologies, a direct catalytic hydration process was also developed in place of the sulfuric acid process traditionally used in the production of ethanol and IPA; this was commercially applied in 1948. Thus, technologies were developed that used catalysts, in particular solid catalysts to achieve direct production, or production of organic intermediates from olefins and aromatic hydrocarbons, and these subsequently became the mainstream in the petrochemical industry.

In the 1950s, polymer production technology took a great leap forward with the discovery of Ziegler-Natta catalysts. The discovery of these organometallic complex catalysts not only became, and continues to be, the key driving force behind advancements in polymer production technology, it also triggered dramatic leaps in the petrochemical industry in terms of production volume. What is notable is that this discovery was made in Germany and Italy, not in the United States, which had been the birthplace of the petrochemical industry. By this point, the United States no longer had sole reign over petrochemical technologies; this was the beginning of new advances through the marriage between American and European technologies.

5.3.1 The American petrochemical industry expands

(1) Olefins

From the 1920s to the 1940s, the growth of the petrochemical industry in the United States was based on olefins, such as those sequestered from petroleum refining waste gas and those obtained from steam cracking ethane and propane in natural gas. By the 1950s, the steam cracking of ethane and propane in natural gas became the mainstream method for producing ethylene in the United States. At the same time, the rapid spread of fluidized catalytic cracking (FCC) led to an increased supply of propylene and butylene, thereby achieving a production system for other olefins in which the key ingredient was waste gas from oil refining.

Naphtha steam cracking was still being used, although it only accounted for a small percentage of olefin production in the United States. In contrast to steam-cracked naphtha gas, steam-cracked ethane gas and oil refining waste gas contained almost no butadiene; accordingly, the supply of butadiene in the United States was obtained via butylene dehydrogenation. Furthermore, the practice of obtaining butadiene from fermentation ethanol was abandoned in peacetime for cost reasons.

(2) Aromatic hydrocarbons

Major changes also occurred in the production of another basic petrochemical, aromatic hydrocarbons, which were supplied exclusively from coal tar during the Second World War. During the war, a process for the catalytic reforming of naphtha was developed and commercialized. Not long afterwards, in 1949, UOP developed the Platforming Process, which used platinum as a catalyst instead of the conventional molybdenum oxide. In no time at all, this became the primary process used for catalytic reforming. In 1952, UOP developed the Udex process to recover aromatic hydrocarbons from reformates (i.e. mixtures of hydrocarbons). It has been known for some time that reformates contain large quantities of aromatic hydrocarbons, but, in contrast to coal tar distillation, reformates contained many azeotropes, meaning that these aromatic hydrocarbons could not be efficiently recovered by distillation. The Udex process enabled the recovery of aromatic hydrocarbons from reformates by skillfully combining extraction with a solvent mixture of glycol and water and extractive distillation. Meanwhile, having peaked around 1950 steel production in the United States began to decline. As a result, coal tar production also began to decline, and manufacturers were becoming unable to cope with the rapidly growing demand for aromatic hydrocarbons needed for polystyrene, nylon and other products. Between 1950 and 1959 in the United States, the source of aromatic hydrocarbons shifted completely from coal tar to reformates and cracked gasoline, obtained from the steam cracking of naphtha. In particular, as the United States relied primarily on the steam cracking of ethane, cracked gasoline supplies were scarce, and aromatic hydrocarbons had to be sourced mainly from reformates.

(3) Industrial organic chemicals

The alcohol production processes that gave birth to the petrochemical industry in the 1920s also experienced major technological innovation in the 1950s. A direct hydration process using a solid catalyst was developed and put into commercial use, replacing the old indirect hydration process using sulfuric acid. With the sulfuric acid process, olefins were reacted with sulfuric acid to create organosulfate, which was then hydrolyzed to obtain alcohol. The diluted sulfuric acid byproduct was concentrated by heating and then reused. In essence, this process was a combination of stoichiometric reactions. By contrast, Shell developed and commercialized a method to synthesize ethanol by using a phosphate-silica catalyst to react ethylene in its gas phase directly with steam in 1948. The same process was also developed by British Petroleum (BP), who achieved the industrial application of it in 1951. Also in 1951, British company ICI commercialized an IPA production method involving a direct reaction of propylene with steam using a tungsten oxide-silica catalyst.

As previously mentioned, manufacturers in the United States were mass producing cumene from propylene and benzene for use in high-octane gasolines. Again in 1951, Hercules Inc. developed a method for the co-production of phenol and acetone from cumene. This process was first applied industrially in Canada in 1953. The following year, it was adopted in the United States and throughout Europe. This was a major innovation that changed how phenol was produced the world over. Compared to past processes, this enabled production under much milder conditions and yielded fewer byproducts; it remains the mainstream process utilized throughout the world to the present day.

(4) Polymers

At the end of the Second World War, the United States government sold off its state-owned synthetic rubber and other factories inexpensively to chemical companies. With the sudden loss of this massive demand from the military, synthetic rubber and a host of other chemical products experienced a temporary decline in production; however, the nation's well-equipped factories did not remain idle for long as the mass consumer demand in the United States was quick to blossom, having been suppressed during the war.

Unsaturated polyester, polytetrafluoroethylene and silicone joined the lineup of polymers in addition to those developed in the 1940s; furthermore, LDPE and polystyrene triggered significant advances in the United States petrochemical industry, having gone into full-scale production for military use during the war and then emerging as all-purpose commercial-use polymers. Following on the heels of nylon, the demand for synthetic fibers acrylic and polyester started growing in the United States in the 1950s. Meanwhile, manufacturers leveraged the advances made in production and molding technologies achieved during the Second World War to bring about even more widespread commercial use of a raft of polymers that had been made primarily from coal since the 1930s, namely, vinyl chloride, phenolic resin, urea resin, methacrylate resin and nylon. Manufacturers began using the EDC process to make vinyl chloride, the raw material for polyvinyl chloride, from ethylene, and the cumene process used to make phenol, the raw material for phenol resin and nylon, and acetone, the raw material for methacrylate resin. Thus, these polymers were incorporated into the petrochemical industry.

Great strides were also achieved in polymer forming technologies during the Second World War. In addition to the conventional techniques of compression molding and calendar molding, the 1950s saw the growth of extrusion molding, which had already been used extensively during the war to produce synthetic fibers, pipes, films, sheets and wire coating, as well as growth in the size of the machinery used. Injection molding, which was already in use before the war for the fabrication of small plastic components, also made leaps after the war, as the size of machinery grew and processes were accelerated and automated. Consequently, the United States petrochemical industry was able to develop rapidly in the postwar years with two thermoplastics, polyethylene and polystyrene, as the main driving force.

5.3.2 The birth and development of the European petrochemical industry

An industry evolved from the mass production of chemicals from coal and fermentation ethanol in the first half of the 20th century in Europe, the birthplace of the modern chemical industry. During the Second World War, coal liquefaction using high-pressure hydrogenation and the production of artificial petroleum via the Fischer-Tropsch process were both carried out on a large scale in Germany. Technologies for large-scale production and continuous operation comparable to those used to make petrochemicals made great strides in Europe; however, since it lacked the abundant supply of natural gas that the United States had, the petrochemical industry did not emerge there until the 1940s.

(1) European energy revolution

In the 1930s, large reserves of oil were discovered in the Middle East. After the Second World War, this crude oil started being exported around the world in large quantities. Given these circumstances, large oil refineries were erected, primarily in the coastal areas of Europe, as part of the United States' Marshall Plan for European reconstruction. Refining oil in oil-consuming areas rather than in oil-producing areas was a major shift, resulting in Europe transitioning from coal to crude oil-based energy. This was the European energy revolution. However, passenger cars had a low penetration rate in Europe, unlike the United States, so the demand for petroleum products focused heavily on heavy fuel oil rather than on gasoline. For this reason, European refineries did not undertake catalytic cracking and catalytic reforming on as large a scale as their American counterparts, nor did they supply large amounts of petroleum waste gas. Nevertheless, refineries in France began producing small volumes of propylene-based solvents from petroleum waste gas in 1949, which can be deemed as the start of petrochemistry in Europe.

(2) Origins of the European petrochemical industry

The full-fledged development of the petrochemical industry in Europe originated with the steam cracking of naphtha, gas oil and other liquid hydrocarbons produced from European refineries to generate olefins and aromatic hydrocarbons. In 1950, British company ICI adopted a superheated steam cracking process from American company Kellogg and built Europe's first naphtha steam cracking plant in Wilton in northeast England, thus forming the beginnings of a petrochemical complex in the area. The United Kingdom was also home to the BP refinery in Grangemouth, northern Scotland, and the Esso Fawely refinery in the suburbs of Southampton, in the south of England. Thus, an increasing number of large petrochemical complexes grew up around large oil refineries. In the early 1950s, France, Italy and the Netherlands also began their own petrochemical industries. Meanwhile, (West) Germany, which had just suffered defeat in the Second World War, remained far behind its European neighbors, and was not able to establish a petrochemical industry until the latter half of the 1950s. In West Germany, reconstruction began with the field of coal chemistry.

Given its origins in the steam cracking of naphtha, the European petrochemical industry was typified by each complex producing an extremely large number of products, since they had to make effective use of the many types of olefins and aromatic hydrocarbons that were co-produced. It was also typified by a large number of joint venture companies backed by American or British oil or chemical companies paired with chemical companies in the various countries of Europe. For instance, in West Germany, BASF joined with Shell to form Rheinische Olefinwerke (ROW), while Bayer joined with BP to establish Erdölchemie to undertake the steam cracking of naphtha; both were fifty-fifty joint ventures. Yet another feature of the industry in Europe was the formation of complexes that included industrial organic chemical and polymer production plants centered around the naphtha steam cracking plants, which themselves were adjacent to oil refineries in the coastal areas. A similar situation emerged in Japan, but not in the United States (see Section 2.5.2)

(3) Successive development of European petrochemical technologies

Europe was home to a large number of companies with top-tier chemical technologies. Therefore, although the industry began with the steam cracking of naphtha, by the time olefins and aromatic hydrocarbons could be supplied in abundance, European petrochemical technologies were being developed in rapid succession.

In the 1950s, European governments were heavily involved in the setting of prices for crude oil and petroleum products, and for a time the pricing system was distorted, as shown in Table 5.3. Accordingly, ethylene production technologies that were developed in the United States were adopted, but that was not all. Soon, a raft of domestic ethylene production technologies, including the Catarole process, sand cracking process, the BASF process and the Hoechst process, were developed and put into commercial use by European companies. Some of these companies co-produced ethylene with not just olefins but also acetylene in an effort to make use of their existing acetylene-based technologies and facilities. However, as pricing for petroleum products normalized and technologies were developed that enabled the production of almost all of the industrial organic chemicals from olefins without having to depend on acetylene, the primary method for producing ethylene transitioned to external heat-pipe steam cracking by the end of the 1960s.

Many important manufacturing technologies for industrial organic chemicals were developed in Europe. Factories began using the Hoechst-Wacker process in 1959 (see Section 6.1.2 (2) 1)). This enabled the production of acetaldehyde through the air oxidation of ethylene. As mentioned in the previous chapter, acetaldehyde was an important intermediate product of carbide and acetylene chemistry, and after the war, it remained one of the two pillars of acetylene chemistry, along with vinyl chloride. The Hoechst-Wacker process spread around the world almost immediately, and in 1962, Union Carbide and other American companies converted their factories to employ this process. Thus, one of the major pillars of acetylene chemistry was undone by the Hoechst-Wacker process.

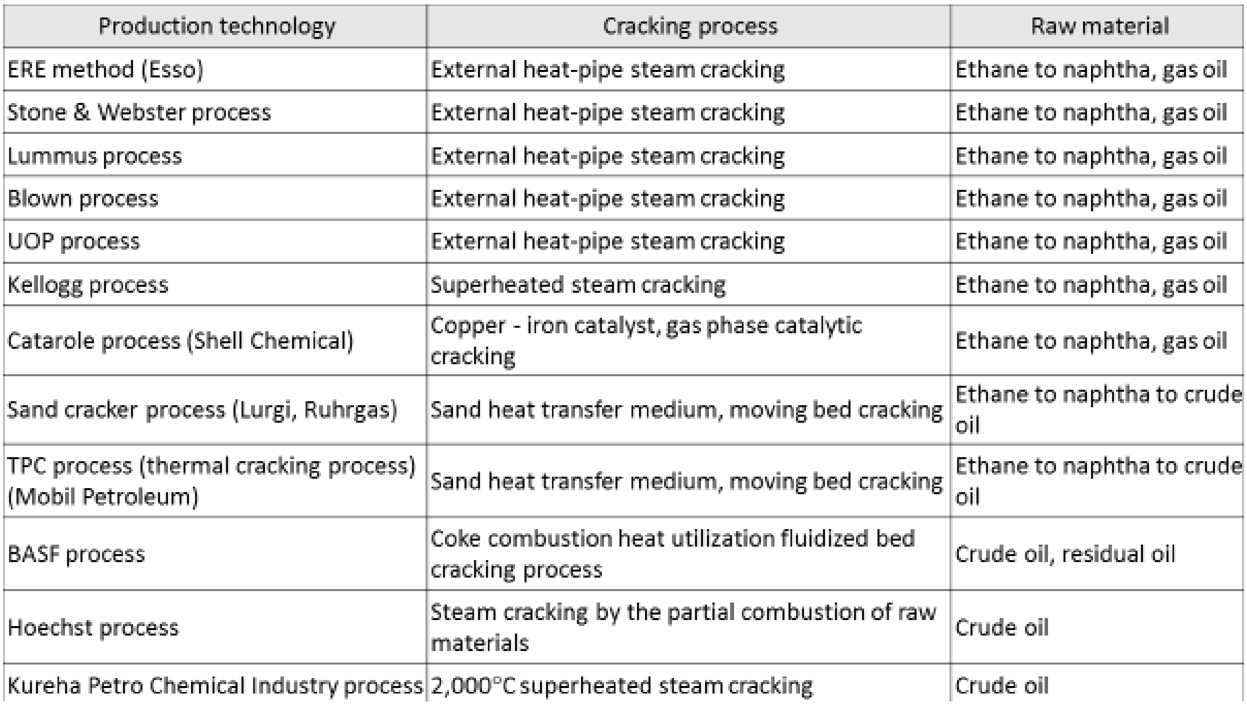
In 1960, a method was developed in the Soviet Union to synthesize vinyl acetate from ethylene and acetic acid in the liquid phase using the same catalyst from the Hoechst-Wacker process; this was put into practical use by British company ICI and American company Celanese in 1965. Not long after, Bayer and others developed a gas phase process.

The biggest contribution from Europe in the history of the petrochemical industry was the discovery of Ziegler-Natta catalysts. It is fair to say that the class of polymers produced using Ziegler-Natta catalysts (namely, HDPE, L-LDPE, PP, EPR, BR, IR, etc.) now account for more than half of all olefin consumption. As has been already mentioned, LDPE was invented by British company ICI in 1933. It was manufactured using radical polymerization under a high pressure (2,000 atmospheres) with oxygen or other initiator. Meanwhile, German chemist Karl Ziegler developed a technique for producing polyethylene at atmospheric pressure using a Ziegler catalyst. This method was put into use by Italian company Montecatini in 1954, West German company Hoechst in 1955, and French company Rhone Poulenc in 1956. This polyethylene, which possessed very different functions and applications than polyethylene produced using a high-pressure process, was called high-density polyethylene (HDPE). In the United States, meanwhile, Phillips Chemical used a chromium oxide catalyst, while Standard Oil (Indiana) used catalysts such as molybdenum oxide in their respective technologies developed in 1957 for the polymerization of HDPE at pressures of 30 to 40 atmospheres. For this reason, manufacturing methods using the Ziegler catalyst are referred to as low-pressure processes, while those used by Phillips and other similar methods are called medium-pressure processes.

However, even with the high-pressure process for producing LDPE (i.e. radical polymerization) and the catalytic polymerization of HDPE, it was not possible to obtain high performance polymers by polymerizing propylene. Italian chemist Giulio Natta successfully obtained high performance PP by developing a method for the stereospecific polymerization of propylene in the presence of a Natta catalyst. Montecatini was the first company to put polypropylene into commercial production. In 1957, it produced resins for plastics at its Ferrara (Italy) plant, and in 1960 it began producing synthetic fibers in its Terni (Italy) plant. Ziegler and Natta catalysts are now collectively referred to as Ziegler-Natta catalysts.[Footnote3][2]

[Footnote3] Refer to Section 3.4.2 (1) for the performance and purposes of various polyethylenes, Section 3.4.3 (1) for PP, Section 3.4.4 (1) and (5) for various rubbers and Section 6.1.3 (1) for polyethylene and PP manufacturing processes and Ziegler-Natta catalysts.

Table 5.3 A variety of ethylene production technologies developed in the 1940s to the 1960s



Production technology	Cracking process	Raw material
ERE method (Esso)	External heat-pipe steam cracking	Ethane to naphtha, gas oil
Stone & Webster process	External heat-pipe steam cracking	Ethane to naphtha, gas oil
Lummus process	External heat-pipe steam cracking	Ethane to naphtha, gas oil
Blown process	External heat-pipe steam cracking	Ethane to naphtha, gas oil
UOP process	External heat-pipe steam cracking	Ethane to naphtha, gas oil
Kellogg process	Superheated steam cracking	Ethane to naphtha, gas oil
Catarole process (Shell Chemical)	Copper - iron catalyst, gas phase catalytic cracking	Ethane to naphtha, gas oil
Sand cracker process (Lurgi, Ruhrgas)	Sand heat transfer medium, moving bed cracking	Ethane to naphtha to crude oil
TPC process (thermal cracking process) (Mobil Petroleum)	Sand heat transfer medium, moving bed cracking	Ethane to naphtha to crude oil
BASF process	Coke combustion heat utilization fluidized bed cracking process	Crude oil, residual oil
Hoechst process	Steam cracking by the partial combustion of raw materials	Crude oil
Kureha Petro Chemical Industry process	2,000°C superheated steam cracking	Crude oil

Ziegler-Natta catalysts have a wide range of applications. Using them in tandem with the stereospecific polymerization of butadiene yielded high performance BR, and in 1960, Phillips Petroleum put this process into practical use in the United States. IR was also developed as a result of the stereospecific polymerization of isoprene, and this went into commercial use in the United States in 1959. In 1958, Montecatini developed an ethylene-propylene copolymer, but was unable to vulcanize it. Then, in 1961, British company Dunlop commercialized EPDM rubber by adding a third component for vulcanization.

(4) The European polymer revolution

In terms of demand, Europe's transition to mass consumerism in the 1950s led to large quantities of polymers being used; this is sometimes called the polymer revolution. This is when a large number of petrochemical-based general-purpose polymers and all-purpose synthetic rubbers were developed and put into practical use in Europe. Examples include ICI's LDPE (the United Kingdom), IG Farben's polyvinyl chloride, polystyrene, and SBR synthetic rubber (Germany), Hoechst's low-pressure HDPE (Germany) and Montecatini's PP (Italy). Therefore, once factories were built for the steam cracking of naphtha, and then olefins and aromatic hydrocarbons could be supplied in abundance in Europe, polymer production rapidly expanded.

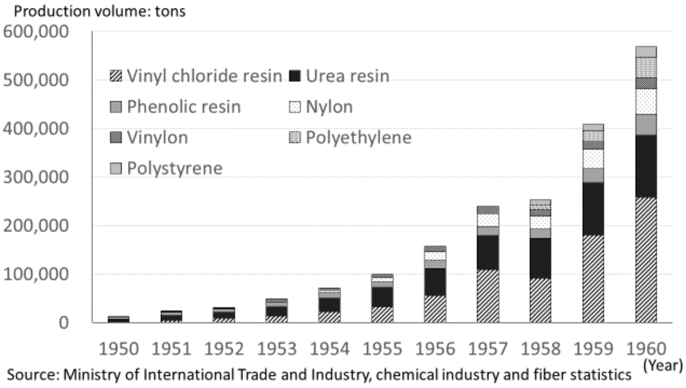
The same was true for synthetic fibers. During the Second World War, Germany produced Nylon 6 from phenol. In 1946, the Calico Printers' Association (the United Kingdom) won approval for its polyester fiber patent. With the transfer of this patent to the rest of the world excluding the United States, ICI began conducting research with an eye on commercialization, and in 1955, ICI's Wilton (the United Kingdom) plant commenced full-fledged production. In the meantime, DuPont, which had received the right to use the patent, started full-scale production in the United States in 1953. DuPont had already begun production of acrylic fibers in 1949, while West Germany's Bayer AG launched production in 1951 in Dormagen (in the outskirts of Leverkusen). In this way, not only did European companies begin producing synthetic fibers soon after their counterparts in the United States, it was often the case that they developed their own technologies instead of relying on technology transfers.

5.3.3 The birth of the Japanese petrochemical industry

In many ways, Japan was in a situation similar to that in Europe. Lacking access to large amounts of oil and natural gas, Japan developed a large-scale chemical industry based on coal and fermentation ethanol before and during the Second World War. Like Germany, Japan had to start from scratch upon its defeat in the war. Reconstruction of the industry started with coal chemistry centering on coal, hydroelectric power, limestone and other domestically available resources.

(1) The advent of Japan’s polymer age

By the late 1940s, Japan had access to an abundance of information about the advancement of the petrochemical industry and utilization of polymer products in the United States. Japan resumed production of the important organic intermediate acetaldehyde from acetylene soon after the end of the war. Not long after that, in the early 1950s, the production of a range of acetylene-based compounds, including vinyl chloride, polyvinyl chloride, vinyl acetate, polyvinyl alcohol, vinylon and methacrylate resin was in full swing. Japan also commenced production of phthalic anhydride, phenol, caprolactam and nylon from coal. The production of urea resins from urea, methanol and formaldehyde generated from coke oven gas and coke-based syngas increased rapidly. Together with celluloid, phenol resins and rayon, which Japan had been producing before the war, vinylon, nylon, polyvinyl chlorides, urea resins and other polymers spread rapidly throughout post-war Japan. LDPE and polystyrene imported from the United States were added to the lineup, and Japan found itself thrust fully into the polymer era even before its petrochemical industry had fully gotten off the ground. As shown in Fig. 5.1, the polymers that were used particularly frequently from the late 1940s to the 1950s were polyvinyl chlorides and urea resins.



Source: Ministry of International Trade and Industry, chemical industry and fiber statistics

Fig. 5.1 Change in production volumes of major synthetic polymers in Japan in the 1950s.

(2) Natural gas kick starts petrochemistry in Japan

As shown in Table 5.4, domestically produced natural gas (primarily methane without ethane or other gases) became the raw material for syngas. From this, Japan Gas Chemical began producing methanol in its Niigata plant in 1952, followed by ammonia and urea in 1957. The following year, Toyo Koatsu began producing methanol from natural gas at its Mobara factory. In terms of how petrochemistry is defined in this study, 1952 can be considered to be the year in which the field came into being in Japan.

Table 5.4 First production of petrochemical products in Japan in the 1950s.

Year	Product	Company, factory
1951	Household mineral oil-based synthetic detergent	Lion Fat and Oil
1952	Methanol from natural gas	Japan Gas Chemical, Niigata
1957	Polystyrene	Monsanto Kasei Kogyo, Yokkaichi; Asahi Dow,Kawasaki
1957	sec-Butyl alcohol, MEK	Maruzen Petroleum, Shimotsu
1957	Ammonia, urea	Japan Gas Chemical, Niigata
1957	IPA, acetone	Nippon Petrochemicals, Kawasaki
1958	Ethylene (naphtha steam cracking)	Mitsui Petrochemical Industries, Iwakuni; Sumitomo Chemical, Oe
1958	Low-density polyethylene (ICIprocess)	Sumitomo Chemical, Oe
1958 1959	Ethylene oxide glycol (SD process) Ethylene oxide glycol (Nisshoku process)	Mitsui Petrochemical Industries, Iwakuni; Nippon Shokubai, Kawasaki
1958	High-density polyethylene (Ziegler process)	Mitsui Petrochemical Industries, Iwakuni

1958	Aromatic hydrocarbons from cracked gasoline (UOP process)	Mitsui Petrochemical Industries, Iwakuni
1958	Polyester fiber	Toyo Rayon, Mishima
1958	Aromatic hydrocarbons from reformates	Mitsubishi Oil, Kawasaki
1958	Hard type alkylbenzene	Nissan Chemical Industries, Ltd., Nagoya
1958	Phenol, acetone (cumene process)	Mitsui Petrochemical Industries, Iwakuni
1958	Terephthalic acid (SD process)	Mitsui Petrochemical Industries, Iwakuni
1959	Acrylic fiber	Mitsubishi Rayon, Otake; Japan Exlan, Saidaiji; Asahi Kasei, Fuji
1959	High-density polyethylene film	Mitsui Chemicals, Nagoya
1959	Non-ionic surfactant	Yokkaichi Chemical Company
1959	Propylene oxide, glycol	Asahi Denka, Oku
1959	Styrene monomer	Mitsubishi Petrochemical, Yokkaichi; Asahi Dow, Kawasaki
1959	Butadiene	Nippon Petrochemicals, Kawasaki
1959	High-density polyethylene (Phillips process), High-density polyethylene (standard process)	Showa Yuka, Kawasaki; Furukawa Kagaku Kogyo, Kawasaki
1959	Nitrile rubber, SBR latex	Zeon Corporation, Kawasaki

Source: Reference [12] and others

Not only did Japan Gas Chemical use domestic resources to produce its methanol, it also used domestic technology in the form of repurposed scrap equipment from an old Imperial Navy fuel factory. At that time, the only other competitors making methanol were using coke oven gas, as they had done since before the war. However, in order to survive, they soon had to switch from the raw materials they were using to natural gas, and then to naphtha and LPG. In this sense, the bold choice of raw materials by Japan Gas Chemical, which was established in 1951, was the precursor of subsequent innovations in petrochemical technologies. Methanol and urea were the key ingredients in urea resins, whose production was skyrocketing.

(3) The run-up to petroleum-based petrochemistry

In Japan, the situation regarding large-scale refineries, which would later become the basis for the establishment of the nation's petrochemical industry, was entirely different from that in Europe. After the war, the occupation forces ordered the shutdown of the refineries along the Pacific coast, and these remained closed for more than four years. In July 1949, the refineries were finally allowed to be reopened after United States occupation policy shifted due to the intensifying Cold War. Nevertheless, many of the refineries did not commence actual operation until 1950. During this time, many of the Japanese oil companies had entered capital and business tie-ups with major Western oil companies.

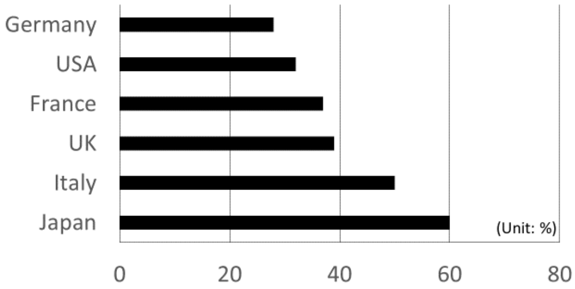
The restarting of the oil refineries combined with Japan's shift towards consuming Middle Eastern crude oil imports served to lay the foundation for the petrochemical industry in Japan. Stimulated by stories of petrochemical breakthroughs from Europe and the United States, Japan's interest in petrochemical commercialization continued to grow. As a result, many plans were devised from the late 1940s onwards to foster the growth of petrochemistry in Japan. However, compared to the mass-production chemical industry that Japan had employed thus far, the petrochemical industry had product categories with a larger number of co-products, and required much vaster expanses of land, which in turn necessitated massive funding. In addition, many new products were not known in the Japanese market (e.g. polyethylene, polystyrene, polyester fibers, acrylic fibers, synthetic rubbers etc.), and companies were often reluctant to enter into production of these alone due to the risks involved. For this reason, Japan needed more time even more so than Europe, for its petrochemical industry to be established. The involvement of the government was also significantly more substantial than in Europe or the United States, and this was a major factor in the length of time it took for plans to reach fruition. In fact, there were many areas of government involvement on several fronts, namely, permits for the sale of former army and navy fuel factories, permits for coastal reclamation, restrictions on foreign capital inflows, low-interest financing from government-affiliated financial institutions and other kinds of aid, and permits for technical transfers. By using these kinds of carrot-and-stick measures, the Japanese government was not only trying to cultivate the petrochemical industry, it was also embarking on a sustained period of intervention, which lasted until the 1980s, with regard to the construction and expansion of facilities, supply and demand and raw material pricing and procurement. This marked the return of the Organic Synthesis Industry Law, as mentioned in the previous chapter. From the 1970s onwards, these kinds of policies were repeated in various developing countries as they nationalized their petrochemical industries, although the periods of government intervention differed greatly from country to country.

In 1957, seven years after the refineries resumed operation, Maruzen Petroleum began using catalytically cracked petroleum waste gas to produce sec-butyl alcohol and MEK from n-butylene at its Shimotsu Plant. Also around this time, Nippon Petrochemicals began using catalytically cracked petroleum waste gas to produce IPA and acetone propylene at its Kawasaki Plant. Some historians identify this as the birth of the petrochemical industry in Japan (Table 5.4). These refineries had catalytic crackers and used the petroleum waste gas they generated themselves. However, as in Europe, the demand for petroleum products in Japan at that time was dominated by heavy fuel oil; accordingly, catalytic cracking and catalytic reforming were not carried out on a very large scale. Therefore, unlike in the United States, the subsequent growth of the petrochemical industry was not based on petroleum waste gas.

That same year, Monsanto Kasei Kogyo produced polystyrene at its Yokkaichi Plant using styrene monomer imported from the United States, while Asahi-Dow did the same at its Kawasaki Plant. The objective behind this was to quickly gain control of the fast growing polymer market, assuming that petrochemical complexes with naphtha steam crackers would soon become able to produce these products. In the 1960s, both companies grew to become leaders in Japan's petrochemical industry.

(4) Steam cracking of naphtha

The full-fledged birth of the petrochemical industry in Japan began with the steam cracking of naphtha (Table 5.4), as it had in Europe. The first steam cracking plant to go online in Japan was Mitsui Petrochemical Industries' Iwakuni Plant. In addition to its polyethylene plant, the company launched plants to produce aromatic hydrocarbons, ethylene oxide and glycol at almost the same time, and its facility for the production of phenol and acetone using the cumene process went into operation several months later. Meanwhile, Sumitomo Chemical's Oe Plant, which started operation in the same year, began producing polyethylene alone. It turned surplus hydrocarbons into syngas using a steam reformer to create the raw material for producing ammonia. Mitsubishi Petrochemical began domestic production of styrene monomer and butadiene at its Yokkaichi Plant, which went into operation the following year. By 1963, five years after the first ethylene plants opened in Japan, the percentage of ethylene consumption dedicated to polyethylene had grown to 60% (see Fig. 5.2), significantly higher than in the United States or Germany. This is likely due to the fact that the products were highly profitable amid the rapid expansion of the polyethylene market. The Japanese petrochemical industry in the 1950s relied almost entirely on ethylene products especially polyethylene, whose market had begun to grow at fever pitch. The management style employed at Sumitomo Chemical's Oe Plant is considered to be typical of the Japanese petrochemical industry in the 1950s.



Source: Reference [8]

Fig. 5.2 Percentage of polyethylene in ethylene consumption in 1963.

5.4 The 1960s: *Sturm und Drang* for petrochemistry

Due to the rapid development of its petrochemical industry, Japan started keeping pace with the United States and Europe by the 1960s, and these three regions became the three dominant forces in the global petrochemical industry. Despite having only just begun at the end of the 1950s, the Japanese petrochemical industry grew so rapidly in the 1960s that it overtook many European countries in ethylene production capacity (including the United Kingdom, which was the first out of the gate in this area). By the end of the 1960s, Japan's petrochemical industry was second only to the United States worldwide.

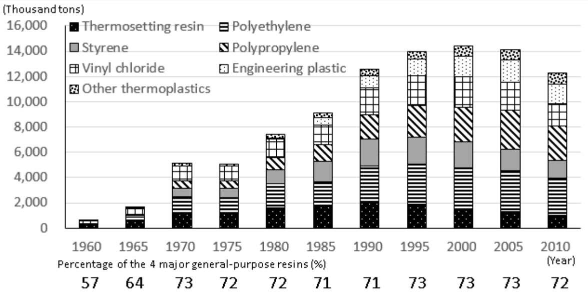
In the 1960s, not only did remarkable technological innovations occur in the field of petrochemistry, but the industry came to form the basis for the chemical industry as a whole. This was truly a period of *Sturm und Drang* for petrochemistry. Having kept up with the times, Japan was fortunate enough to make its way into the global arena. The following sections will primarily discuss the Japanese petrochemical industry, for which statistics are readily available.

5.4.1 The Japanese polymer revolution

Polymers gradually permeated the United States market between the 1930s and the 1950s, and spread at an explosive rate in Japan from the mid-1950s into the 1960s. Thus, Japanese society truly felt the impact of what could be called a polymer revolution.

Supermarkets first appeared in Japan in the mid-1950s. As in the United States, supermarkets were an essential driver of polymer demand due to the massive amount of films and trays used for wrapping foods and the plastic daily goods sold. In other words, the growth of supermarkets went hand in hand with increased polymer consumption. Plastics were used for beer containers, fertilizer and rice bags, and flexible containers used for transporting bulk items. Plastics were also used in televisions, radio receivers, refrigerators, washing machines and other trademark appliances of the postwar period of rapid economic growth. Furthermore, plastics were essential as agricultural materials, such as plastic greenhouse films, and construction materials, such as sewer pipes, rain gutters and corrugated roofing. Furthermore, glue, coating and other chemical products that were previously made from natural polymers or polymers derived from the oxidation of unsaturated fats and oils came to be comprised mainly of synthetic polymers. A lifestyle in which plastics came to be commonplace and were consumed *en masse* took root in Japan in the 1960s.

The production of plastics in Japan topped 100,000 tons in the mid-1950s, before increasing more than fivefold to nearly 600,000 tons just five years later in 1960. A further ten years later, production leapt almost ninefold to 5 million tons, as shown in Fig. 5.3. Due to its light weight, low cost, water resistance and excellent moldability, there was a surge in demand for plastic as it came to replace a wide range of existing materials, including paper (e.g. wrapping paper and boxes), natural rubber (e.g. wire coatings and hoses), celluloid/cellophane (e.g. packaging and daily necessities), metal (e.g. daily necessities and pipes), glass (e.g. containers and daily necessities) and pottery (e.g. containers and daily necessities). From the 1970s to the present day, the four main general-purpose resins (polyethylene, PP, styrene-based resin and PVC) account for more than 70% of all plastics, as shown in Fig. 5.3.



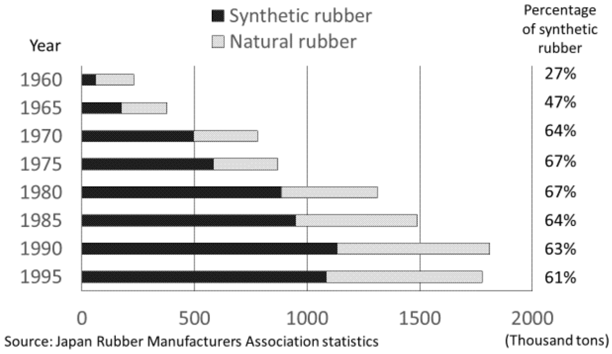
Note: Engineering plastic system means the total of PA, PC, POM, PET, PBT, PPE, fluorine resin.

Source: Japan Plastics Industry Federation statistics (partly modified)

Fig. 5.3 Changes in plastic production volumes in Japan.

Due to the difficulty in using statistics to present the overall picture of how plastic permeated the entire realm of existing materials, let us outline its permeation into two fields: rubber, in the form of synthetic rubber, and textiles, in the form of synthetic fibers.

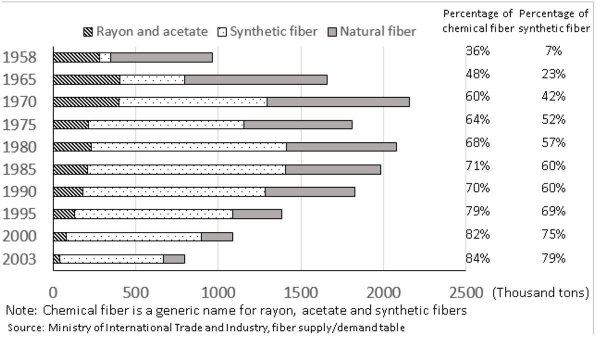
In postwar Japan, the domestic production of synthetic rubber was significantly delayed, having been banned for several years by the United States occupying forces. In 1959, synthetic rubber production finally began with Zeon, which was a joint venture between the American company B. F. Goodrich Chemicals and the Furukawa Electric Group. The use of synthetic rubber in Japan dates back to the early 1950s. In 1960, 52,000 tons of the product were imported, while 23,000 tons were produced. Accordingly, as Fig. 5.4 shows, the ratio of synthetic rubber to new rubber consumption in 1960 was 27%. In 1965, synthetic rubber production reached 161,000 tons versus 30,000 tons of exports and 27,000 tons of imports, bringing the ratio of synthetic rubber to new rubber consumption to 47%. In 1970, this ratio increased to 64% on the back of 698,000 tons of synthetic rubber production. From then until the present day, the ratio has steadily remained around 60%.



Source: Japan Rubber Manufacturers Association statistics

Fig. 5.4 Change of consumption volume of new rubber in Japanese rubber molding industry.

Let us turn our attention to textiles. Japan was a massive producer of rayon before the Second World War, and the rayon industry was one of the first to recover after the war. As Fig. 5.5 shows, by 1965, rayon, acetate and other chemical fibers containing synthetic fibers accounted for 48% of all textiles; these fibers came to rival almost all of the natural fibers, such as cotton, wool, hemp and silk. Synthetic fibers accounted for just under half of all chemical fibers. At that point in time, the biggest products were rayon and acetate, which used natural polymers. However, the latter half of the 1960s saw a boom in the synthetic fibers industry. By 1970, the textile industry was 40% synthetic fibers, 20% rayon and acetate, and 40% natural fibers: synthetic fibers had finally usurped the top position in the market. After that, the ratio of synthetic fibers continued to increase, and now they account for over 80% of fiber production in Japan.



Note: Chemical fiber is a generic name for rayon, acetate and synthetic fibers

Source: Ministry of International Trade and Industry, fiber supply/demand table

Fig. 5.5 Changes in production volumes of thread in Japan by material.

5.4.2 The shift from coal-based to petroleumbased products

Rayon and coal chemistry saw postwar production top their prewar peak in the chemical industry, which existed before the petrochemical industry. As has been already mentioned in the previous section, a major shift from rayon to synthetic fibers occurred in the late 1960s. This section discusses the shift from coal-based to petroleum-based products.

(1) Aromatic hydrocarbons

The shift from coal-based to petroleum products began with aromatic hydrocarbons. Japan began producing aromatic hydrocarbons from cracked gasoline and reformates in 1958, about five years behind the United States. In 1958, phenol was produced by applying the cumene process to benzene obtained from cracked gasoline.

In the same year, production began on terephthalic acid (SD process), the raw material for polyester fiber. This was a superior process that enabled the one-stage manufacturing of terephthalic acid by the direct oxidation of paraxylene. Developed by Scientific Design (SD) in 1955, this process was first used in commercial production in

1958, after testing by Amoco. Accordingly, production in Japan began at the same time as production in the United States. Paraxylene, the raw material used in this process, was difficult to obtain from coal tar, but readily accessible from cracked gasoline and reformates. Mixed xylenes, paraxylene, terephthalic acid and polyester fibers were the aromatics that came to represent petrochemistry. As Table 5.5 shows, the production of paraxylene in Japan began in 1960, just two years after terephthalic acid. Domestic production of paraxylene did not begin until the production of terephthalic acid from imported paraxylene had properly commenced.

Table 5.5 First production of petrochemical products in Japan in the 1960s

Year	Product	Company, factory
1960	Phthalic anhydride (o-xylene method)	Nippon Shokubai, Suita
1960	2-Ethylhexanol, iso-butanol (oxo process)	Mitsubishi Chemical Industries, Yokkaichi
1960	Styrene-butadiene rubber (SBR)	Japan Synthetic Rubber, Yokkaichi
1960	p-Xylene	Maruzen Petroleum, Matsuyama; Mitsui Petrochemical Industries, Iwakuni
1960	Alkylphenol	Maruzen Petroleum, Shimotsu
1961	Polypropylene glycol	Sanyo Yushi
1961	Polycarbonate resin	Teijin Kasei, Matsuyama
1961	Petroleum resin	Mitsui Petrochemical Industries, Iwakuni
1961	AS resin	Dainippon Celluloid, Sakai, Mitsubishi Monsanto Kasei, Yokkaichi
1962	o-Xylene	Maruzen Petroleum, Matsuyama
1962	Epoxy resin	Mitsubishi Petrochemical, Yokkaichi
1962	Polypropylene fiber	Toyo Rayon, Shiga
1962	Caprolactam (photonitrosation) process	Toyo Rayon, Nagoya
1962	Polypropylene resin	Mitsui Chemicals, Otake
1962	Acetaldehyde (Hoechst-Wacker process)	Mitsui Petrochemical Industries, Iwakuni otake
1962	Acetate, butyl acetate (naphtha direct oxidation process)	Dainihonkasei, Otake
1962	Ethanolamine	Nippon Shokubai, Kawasaki
1962	Acrylonitrile (Sohio process)	Asahi Kasei, Kawasaki
1962	Alkylbenzene	Nihon Sekiyu Senzai, Kawasaki
1963	Acrylamide (sulfuric acid hydration process)	Mitsubishi Chemical Industries, Kurosaki
1963	ABS resin	Hamano Seni Kogyo, Urawa
1963	Methyl isobutyl ketone (MIBK)	Mitsui Petrochemical Industries, Iwakuni otake

Source: Reference [12] and others

The production of phthalic anhydride from orthoxylene also began in 1960 (Table 5.5). The demand for phthalic anhydride was growing rapidly at the time as a raw material for phthalic ester (polyvinyl chloride plasticizers). This was a typical coal-based chemical product. Naphthalene, an intermediate that was originally obtained from coal tar at the end of the 19th century and used as a synthetic dye, was used to stoichiometrically produce oxidants, such as fuming sulfuric acid. In the 1910s, a process was developed to enable the oxidation of naphthalene with a solid catalyst (vanadium pentoxide). In 1945, an o-xylene oxidation process was put into commercial use in the United States using the same vanadium pentoxide catalyst. It took Japan 15 more years to make the switch from coal-based to petroleum products, despite the fact that the technologies were developed proprietarily. This is because the production of mixed xylenes and o-xylene did not begin until much later. Consequenly, the first phthalic anhydride produced in Japan used imported orthoxylene, although production was domesticated in 1962 following a spike in o-xylene imports.

Ever since the commercial introduction of a process to manufacture nylon from caprolactam, phenol was used as the raw material used to make caprolactam. Phenol had been previously produced from benzene obtained from coal tar, but when production via the cumene process began in 1958 it, too, became a petrochemical product. Meanwhile, Toyo Rayon developed a proprietary process for manufacturing caprolactam from cyclohexane, which was cheaper than phenol. This process was called photonitrozation, and it was industrialized in 1962 (Table 5.5). This cyclohexane was made by hydrogenating benzene. The production of benzene from cracked gasoline and reformates began in the late 1950s, meaning that the switchover to petrochemicals as raw materials was already in progress. Cyclohexane, a non-aromatic cyclic hydrocarbon, was also a prototypical petrochemical. Around this same time, several other processes not involving photonitrosation for manufacturing caprolactam from cyclohexane were developed in Europe and the United States, and the transition from phenol to cyclohexane continued. These Western technologies were adopted in Japan from the latter half of the 1960s onward. Soon, caprolactam manufacturers other than Toyo Rayon began using cyclohexane, and this quickly stepped up the pace at which the transition to petrochemical methods progressed. Between 1963 and 1969, a number of companies successively started reducing benzene to create cyclohexane.

(2) Transition from carbide-acetylene chemistry

In the 1960s, new petrochemical technologies based on olefins were developed in rapid succession. These technologies were almost immediately adopted by Japanese companies, and at the same time, domestic technologies were also developed. This meant that carbide-acetylene chemistry had all but disappeared in Japan by the end of the 1960s.

1) Oxo alcohols

As shown in Table 5.5, the conversion of acetylene from a chemical to a petrochemical product began with the production of 2-ethylhexanol by the oxo process in 1960. 2-ethylhexanol is the raw material used to create the polyvinyl chloride plasticizer called dioctyl phthalate (DOP). Previously, this had been synthesized from acetaldehyde, an important intermediate in acetylene chemistry. The production of 2-ethylhexanol by the oxo process involves synthesis from butyraldehyde, itself obtained from propylene (see Section 3.4.3 (6)). Furthermore, this process was proprietarily developed by Mitsubishi.Chemical Industries (now Mitsubishi Chemical).

2) Acetaldehyde, acetic acid and vinyl acetate

In 1962, the Hoechst-Wacker process for synthesizing acetaldehyde from ethylene was introduced into Japan and put into commercial use. The Hoechst-Wacker process was first commercialized in Germany in 1959, and was later adopted throughout Europe. In 1962, it was commercialized in the United States and Canada via technical transfer. Mitsui Petrochemical Industries adopted the technology the same year, followed by Daikyowa Sekiyu Kagaku in 1963, Kasei Mizushima and Chisso Petrochemical in 1964 and Tokuyama Sekiyu Kagaku in 1965. All of these companies launched ethylene-process plants, which were capable of achieving much higher capacity than the conventional acetylene-based plants. With this shift, companies that had previously manufactured acetic acid from acetylene and acetaldehyde began either investing in producers who used the ethylene process to manufacture acetaldehyde or procuring their acetaldehyde from these producers. In 1962, 93% of acetaldehyde was manufactured from acetylene; this had nosedived to 29% by 1965 and 20% by 1967. By 1969, synthetic acetic acid was no longer being produced from acetylene at all. In 1962, a process for producing acetic acid by the direct oxidation of naphtha was commercialized.

Companies that had previously produced vinyl acetate using acetylene also began switching technologies *en masse* in 1967. In 1968, Tokuyama Sekiyu Kagaku and Kurashiki Rayon switched to using ethylene to produce vinyl acetate, followed by The Nippon Synthetic Chemical Industry and others in 1969. Between 1970 and 1986, the production of vinyl acetate from acetylene gradually dwindled to zero.

3) Acrylonitrile

Acrylonitrile had been used for many years in the synthetic rubber called NBR. The early 1960s saw a spike in demand for the polymer for use in acrylic fibers and ABS resins. The method for producing acrylonitrile had undergone several transformations; at that time (the end of the 1950s) it was being produced from acetylene and hydrogen cyanide. Hydrogen cyanide could be made in various ways: from ammonia, methane and air using the Andrussow process, or from methanol, carbon monoxide and ammonia using the formamide method, to name just two. By contrast, the Sohio process developed in 1958 was a superior process that enabled the production of acrylonitrile directly from propylene, ammonia and air. In 1962, the Sohio process for acrylonitrile productions was put into commercial use in Japan as well. In the early 1960s, Japan's acrylonitrile producers began switching to this process in rapid succession. Japan experienced the quickest penetration of the Sohio process out of any country in the world, and it became a voracious consumer of propylene generated as a byproduct of naphtha steam cracking.

4) Vinyl chloride

After the Second World War, massive amounts of acetylene came to be used for vinyl chloride, forming the driving force that saw acetylene chemistry grow by leaps and bounds, both in Japan and the West. Compared to the manufacturing of vinyl chloride from acetylene, manufacturing from ethylene was somewhat more complex, so in Japan, like many other countries, vinyl chloride was the last compound to make the switch from acetylene chemistry to petrochemistry. This transition can be seen in Table 5.6.

Table 5.6 First production of petrochemical products in Japan in the late 1960s

Year	Product	Company, factory
1964	Vinyl chloride (mixed gas process)	Kureha Petro Chemical Industry, Nishiki
1964	Caprolactam (new Inventa process)	Mitsubishi Chemical Industries, Kurosaki
1964	Vinyl chloride (EDC process)	Central Chemical, Kawasaki/Zeon Corporation, Takaoka; Shunan Petrochemical, Tokuyama; Mitsui Chemicals, Nagoya
1964	Acetic acid (Distiller's method naphtha direct oxidation process	Dainihonkasei, Otake
1964	Acetone (Wacker process)	Daikyowa Sekiyu Kagaku, Yokkaichi
1964	Butadiene rubber	Japan Synthetic Rubber, Yokkaichi; Asahi Kasei, Kawasaki
1965	Perchlorethylene, trichlorethylene (EDC process)	Kanto Denka Kogyo, Mizushima
1965	Synthetic ethanol	Japan Synthetic alcohol, Kawasaki
1965	Butadiene (GPBprocess)	Zeon Corporation, Tokuyama
1965	Higher alcohol (Ugine Kuhlmann process, France)	Nissan Petrochemicals, Chiba
1965	Ethylene-vinyl acetate copolymer resin (EVA)	Mitsui Polychemicals, Otake
1966	Linear alkylbenzene (LAB)	Nissan Petrochemicals (Nissan Conoco), Chiba
1966	Acrylic acid ester (AN hydrolysis process)	Mitsubishi Petrochemical, Yokkaichi
1966	Vinyl chloride (oxychlorination process)	Toyo Soda Manufacturing, Nanyo
1966	Epichlorohydrin	Asahi Glass, Yodogawa
1967	Acrolein (propylene process)	Daicel Chemical Industries, Otake
1967	Vinyl chloride (GPA process)	Zeon Corporation, Takaoka
1967	Vinyl acetate (ethylene process)	Tokuyama Sekiyu Kagaku, Nanyo
1968	n-Paraffin	Nikko Yuka
1968	Polyacetal resin	Polyplastics, Fuji
1968	Butyl rubber	Japan Butyl, Kawasaki
1968	Mixed xylene isomerization, m-xylene	Japan Gas Chemical, Mizushima
1969	Solution polymerization SBR	AA Chemical, Oita
1969	Toluene disproportionation	Toyo Rayon, Ukishima

Source: Reference [12] and others

Conventionally, vinyl chloride was produced by causing a reaction between acetylene and hydrogen chloride. When using ethylene, on the other hand, ethylene has to be reacted with chlorine to create ethylene dichloride (EDC), which is then subjected to gas-phase cracking to yield vinyl chloride (i.e. the EDC process). Several companies had put the EDC process into commercial use.Since the thermal cracking in the EDC process yielded large amounts of byproduct hydrochloride with the same number of moles as vinyl chloride, the companies needed to secure consumers for this hydrochloride. However, the issue of what to do with the surplus hydrogen chloride was resolved by running this process in parallel with the conventional process involving a reaction between acetylene and hydrogen chloride. One mole of acetylene would eventually react with ethylene and chlorine to create two moles of vinyl chloride (i.e. the acetylene-ethylene combination process). However, because this method required both ethylene and acetylene, it was not able to take advantage of the merits of the ongoing shift to petrochemistry. Around 1960, all three processes – the acetylene process, the EDC process and the acetylene-ethylene combination process – were being used in the United States. In Japan, Central Chemical, Shunan Petrochemical and Mitsubishi Monsanto Kasei all opened factories using the acetylene-ethylene combination process in 1964.

Also in 1964, Kureha Chemical Industry put a process into commercial use that it had developed to produce vinyl chloride from a mixture of acetylene and ethylene gases obtained through the flame cracking of naphtha. (This plant remained in operation until 1982.) In 1967, Zeon opened a plant using the GPA process, which was based on the same mixture of acetylene and ethylene gases. (This plant remained in operation until 1979.) Later, in 1970, Kureha Chemical Industry opened a plant to produce vinyl chloride from a mixture of acetylene and ethylene gases obtained through the superheated steam cracking of crude oil. (This plant remained in operation until 1978.) As this shows, several ways to manufacture vinyl chloride were put into use in Japan, many of which were developed domestically.

In an effort to fundamentally solve the problem of what to do with the hydrogen chloride byproduct of vinyl chloride production, oxy-chlorination was developed and put into commercial use in the United States in 1965. Oxy-chlorination employs a copper chloride catalyst to generate EDC and water from a mixture of ethylene, hydrogen chloride and oxygen (or air). When combined with the existing EDC process, this process eventually produces vinyl chloride and water from ethylene, chlorine and air. Since oxy-chlorination uses absolutely no acetylene, this process triggered a complete shift to production using petrochemical methods. Oxy-chlorination quickly made its way around the globe. In Japan, companies such as Toyo Soda Manufacturing (now Tosoh), Tokuyama Soda (now Tokuyama), Toyo Koatsu Industries (now Mitsui Chemicals), and Toagosei Chemical Industry (now Toagosei) all developed oxy-chlorination processes using domestic technology. Until then, the petrochemical industry had relied heavily on technical transfers; this was the first major example of companies adopting technologies developed in Japan. Starting with the adoption of oxy-chlorination at Toyo Soda’s Shin-nanyo Plant in 1966, a raft of Japanese companies began putting the process into use. With this, the share of acetylene-based vinyl chloride production fell sharply from 76% in 1967 to just 18% in 1970.

Oxy-chlorination, which uses hydrogen chloride and oxygen to chlorinate hydrocarbons, was originally the first step in the Raschig process for phenol production,a technology developed in the 1930s to create chlorobenzene from benzene. Thirty years later, the very same process was applied to ethylene. Immediately, numerous companies in Japan and the West could use their own technologies to develop many related processes.

5) Chlorinated solvents

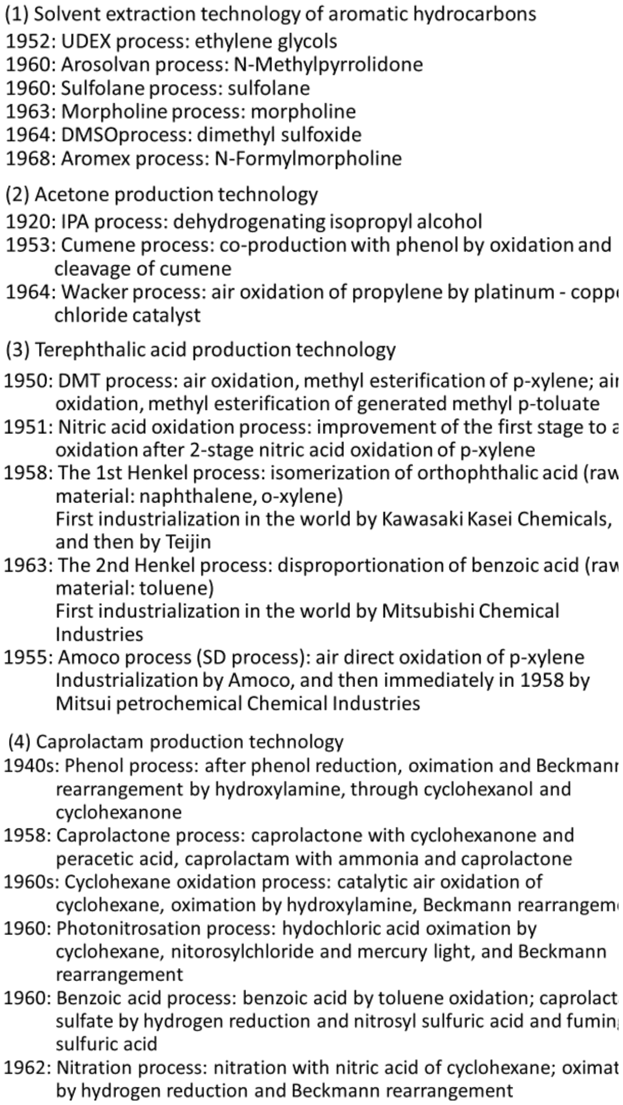
Another example of the shift from acetylene chemistry to petrochemistry was the adoption of processes to manufacture perchloroethylene and trichloroethylene from EDC in 1965.

By the end of the 1960s, the production of chemical products from acetylene had declined significantly in Japan, and other than a small handful of exceptions, no major acetylene products remained in the 1970s. By the 1980s, the industry based on acetylene chemistry had all but vanished. In the United States, the birthplace of petrochemistry, acetylene chemistry surprisingly held on until around the year 2000, when the last acetylene-based vinyl chloride plant was shut down.

5.4.3 Vigorous technological innovation and upsizing

As previously mentioned, the production of alcohols on the petrochemical methods shifted to the direct hydration from sulfuric acid in the 1950s. During the 1960s, similar petrochemical processes were developed in rapid succession, thus spurring an intensive burst of innovation in which the mainstream industrial processes changed dramatically over a short period of time. Table 5.7 shows examples of these kinds of manufacturing processes, including technologies for the extraction of aromatic hydrocarbons and the production of acetone, terephthalic acid and caprolactam. In addition to these, several other competing technologies were developed in the 1960s, such as those for butadiene extraction and hydrogenating dealkylation to obtain benzene from toluene and xylene.

Table 5.7 Cases of intensified competition of manufacturing methods in the petrochemical industry in the 1960s

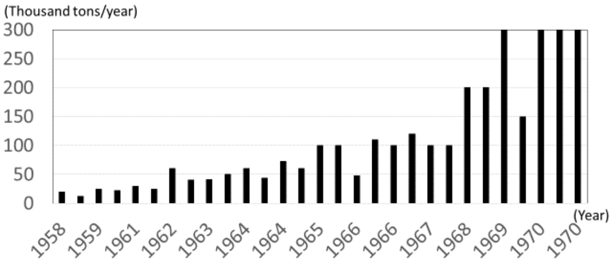


(1) Solvent extraction technology of aromatic hydrocarbons
1952: UDEX process: ethylene glycols
1960: Arosolvan process: N-Methylpyrrolidone
1960: Sulfolane process: sulfolane
1963: Morpholine process: morpholine
1964: DMSOprocess: dimethyl sulfoxide
1968: Aromex process: N-Formylmorpholine

(2) Acetone production technology
1920: IPA process: dehydrogenating isopropyl alcohol
1953: Cumene process: co-production with phenol by oxidation and cleavage of cumene
1964: Wacker process: air oxidation of propylene by platinum - copp chloride catalyst

(3) Terephthalic acid production technology
1950: DMT process: air oxidation, methyl esterification of p-xylene; ai oxidation, methyl esterification of generated methyl p-toluate
1951: Nitric acid oxidation process: improvement of the first stage to oxidation after 2-stage nitric acid oxidation of p-xylene
1958: The 1st Henkel process: isomerization of orthophthalic acid (raw material: naphthalene, o-xylene)
First industrialization in the world by Kawasaki Kasei Chemicals, and then by Teijin
1963: The 2nd Henkel process: disproportionation of benzoic acid (raw material: toluene)
First industrialization in the world by Mitsubishi Chemical Industries
1955: Amoco process (SD process): air direct oxidation of p-xylene
Industrialization by Amoco, and then immediately in 1958 by Mitsui petrochemical Chemical Industries

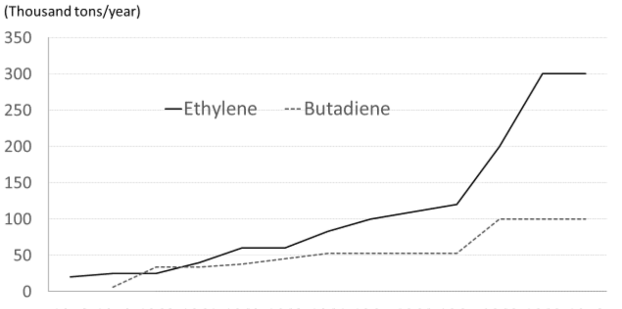
(4) Caprolactam production technology
1940s: Phenol process: after phenol reduction, oximation and Beckman rearrangement by hydroxylamine, through cyclohexanol and cyclohexanone
1958: Caprolactone process: caprolactone with cyclohexanone and peracetic acid, caprolactam with ammonia and caprolactone
1960s: Cyclohexane oxidation process: catalytic air oxidation of cyclohexane, oximation by hydroxylamine, Beckmann rearrangem
1960: Photonitrosation process: hydochloric acid oximation by cyclohexane, nitorosylchloride and mercury light, and Beckmann rearrangement
1960: Benzoic acid process: benzoic acid by toluene oxidation; caprolact sulfate by hydrogen reduction and nitrosyl sulfuric acid and fumin sulfuric acid
1962: Nitration process: nitration with nitric acid of cyclohexane; oximat by hydrogen reduction and Beckmann rearrangement



Note: Capacity at operation starts for each Japanese ethylene plant up to 1970 (Excluding modified capacity after the startups. Increased capacity obviously planned at the openings, however, was included here.)
Source: Reference [9]

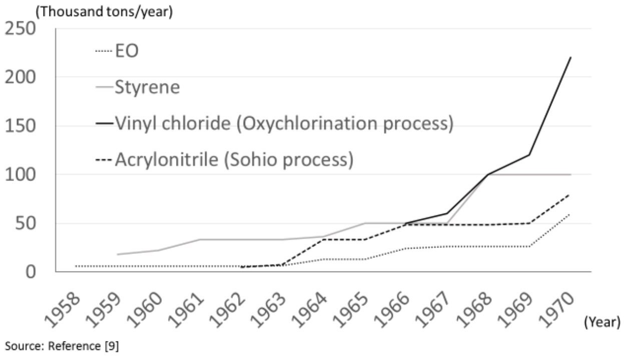
Fig. 5.6 Ethylene capacity per plant around the 1960s.

Another noticeable facet of the 1960s was the progressive upsizing of petrochemical facilities, which is exemplified by the change over time in per-plant ethylene production capacity, as shown in Fig. 5.6. Four plants completed at the end of the 1950s, had an initial average annual capacity of 20,000 tons. The average for the 10 plants completed between 1961 and 1964 jumped to 48,000 tons, while the average for the 10 plants that came online between 1965 and 1968 was 118,000 tons. Furthermore, the average for the five plants opened between 1969 and 1970 was 270,000 tons. In around 10 years, plant capacity had expanded more than fivefold.



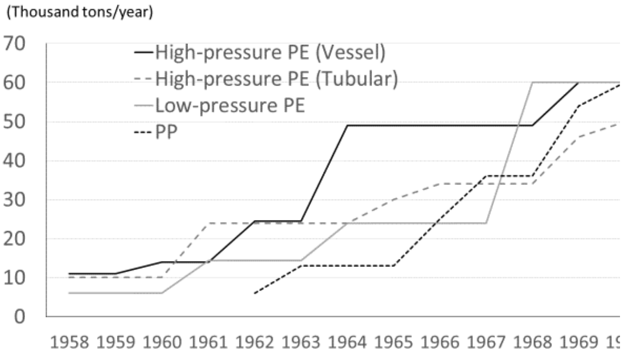
Source: Reference [9]

Fig. 5.7 Change in maximum capacity for each petrochemical plant product in Japan (basic petrochemicals).



Source: Reference [9]

Fig. 5.8 Change in maximum capacity for each Japanese petrochemical plant product (industrial organic chemicals).



Source: Reference [9]

Fig. 5.9 Change in maximum capacity for each petrochemical plant product in Japan (polymers).

In pace with the increase in ethylene plant capacity, the per-plant capacity also increased at plants for basic petrochemicals, organic industrial products and polymers. Figure 5.7 shows the change in maximum capacity for ethylene and butadiene, Fig. 5.8 shows the same for ethylene oxide, styrene, vinyl chloride and acrylonitrile and Fig. 5.9 shows the same for LDPE, HDPE and PP. In the 1950s alone, petrochemical plant capacity had already outstripped the existing capacity of coal-based chemical plants to that point in time. Over the next 10 years, the scale of this upsizing grew even more massive. The primary reason for this upsizing was the pursuit of economies of scale. Since construction expenses increase by an exponent factor of 0.6 compared to plant capacity, the bigger the plant, the cheaper the cost of construction per unit of capacity would become; accordingly, upsizing helped to achieve significant cost reduction.

In the latter half of the 1960s, the major technical factor underlying the successful upsizing of steam cracking plants was the adoption of centrifugal compressors. The same held true for large gas compression facilities, such as ammonia and methanol plants. Furthermore, the 1960s saw the incorporation of transfer line heat exchangers (TLEs) into steam cracking plants. These exchanged the heat of high-temperature steam-cracked gas to enable heat recovery and production of high-temperature (high-pressure) steam, which was used to drive the centrifugal compressors. The widespread adoption of these devices contributed to the upsizing of steam-cracking plants while also decreasing their energy consumption and operating costs.

5.4.4. Integrated usage of non-ethylene olefins and aromatic hydrocarbons

Although the petrochemical industry originated in the United States, there it was primarily a chemical industry driven by ethylene. In Europe and Japan, however, the industry developed based on the steam cracking of naphtha. Accordingly, this required the integrated usage of non-ethylene olefins and aromatic hydrocarbons found in cracked gasoline. For ethane-based steam cracking, the mainstream process in the United States, all that was needed was ethylene production. If a producer needed propylene and butylene, they only had to refine the required quantities from FCC waste gas. Likewise, aromatic hydrocarbons could be extracted in the necessary quantities from reformates. The steam cracking of naphtha, however, produced various other non-ethylene olefins as well. Even at the modern naphtha steam cracking plants with higher ethylene yields, the amount of ethylene generated only amounts to one-third the amount of the naphtha used. The naphtha steam cracking plants in the 1960s yielded even lower amounts of ethylene than this. Accordingly, these plants also produced large quantities of basic non-ethylene petrochemical products. The more these naphtha steam cracking facilities were enlarged, the more important it became to effectively utilize these non-ethylene byproducts.

In 1960, the only major consumers of propylene were plants that produced isopropyl alcohol and alkylbenzene (which used propylene tetramer). Later in the 1960s, however, more uses for the compound were developed. By 1970, PP, propylene oxide (polyurethane), acrylonitrile, oxo alcohols (butyl alcohol, 2-ethyl hexanol, etc.), cumene and other compounds had grown to account for almost as much propylene consumption as isopropyl alcohol. Meanwhile, propylene tetramer, the negative aspects of which are described in the next section, experienced a reduction in production as the demand for it decreased.

Butadiene, the C4 olefin obtained in the highest quantity from the steam cracking of naphtha, had been used to make synthetic rubber since the 1940s. In the 1960s, various more effective extractive distillation processes were developed to take the place of conventional extraction. One of those processes, the GPB process developed by Japanese company Zeon, is an example of a domestic technology that was exported around the globe. Nevertheless, there still remained a lack of demand for C4 butylenes other than butadiene in the 1960s.

The demand for benzene, paraxylene and o-xylene from cracked gasoline skyrocketed. Meanwhile, there was little demand for m-xylene and toluene, but with the commercial application of isomerization and disproportionation, these aromatic hydrocarbons also came to be effectively utilized within the petrochemical industry.

Thus, the 1960s was a time of significant growth for propylene, butadiene and aromatic hydrocarbons as effective ways were developed and adopted to utilize these ethylene co-products of naphtha steam cracking.

5.4.5 Advancements in petrochemistry in the chemical industry

The petrochemical industry grew into a major supplier of hydrocarbon solvents, various industrial organic chemicals and polymers for the chemical industry. Accordingly, the chemical industry as a whole came to be closely linked to the petrochemical industry. Examples of the shift from chemical to petrochemical methods have already been mentioned for the rubber molding and chemical fiber sectors. The 1960s was a time when a wide-range of sectors in other areas also shifted to petrochemistry.

(1) The shift to petrochemistry in chemical industries using petrochemical products

At its onset, the detergent industry originally used fats and oils as raw materials. Before the Second World War, higher alcohols were produced through the high-pressure hydrogenation of fats and oils; these were sulfated to create mild detergents, such as sulfuric acid ester salts.Having suffered a soap shortage during First World War due to a lack of fats and oils, Germany was one of the first countries to begin researching coal chemistry-based synthetic surfactants. By the 1930s, it had begun producing alkylnaphthalenesulfonic acid soda. Production of alkylnaphthalenesulfonic acid soda began in the United States as well, where it was sold as a synthetic detergent. In 1946, after the war, Standard Oil (California) subsidiary company Oronite developed alkylbenzenesulfonic acid soda, which was sold and popularized by P&G. In Japan, the production of alkylbenzene began in 1958, and the production of this and other synthetic detergents soared as electric washing machines became more commonplace. Alkylbenzene is produced by causing a reaction between tetramerized propylene, also known as dodecene, and benzene. Meanwhile, the production of non-ionic surfactants from domestically sourced ethylene oxide began in 1959. In the 1960s, the primary product of the detergent industry shifted from soap to synthetic detergent, which contributed greatly to the transition from fats and oils to petrochemical-based methods.

The same trend occurred in the coating industry. The coating industry originally used drying and semi-drying oils as raw materials, including unsaturated fatty acids. Before the war, the industry had started using alkyd resins made from drying and semi-drying oils and phthalic anhydride as resins for coating. Phthalic anhydride was created by oxidizing the naphthalene obtained from coal tar. After the Second World War, coating manufacturers began using amino-alkyd resins, polyvinyl chlorides and unsaturated polyester resins as resins for coating, all of which were products of coal chemistry. In the 1960s, the petrochemical industry began producing excellent coating resins such as epoxy, acrylic and polyurethane resins. Phthalic anhydride also made the jump from using a coal-based raw material (naphthalene) to a petroleum-based raw material (orthoxylene). This meant that alkyd resins and unsaturated polyester resins were also now petrochemical products. Thus, the coating industry also shifted from a fats and oils based industry to a petrochemistry-based industry.

The adhesives industry began with natural polymers such as glue and paste. Before the war, the industry used phenolic resin, but shifted to using large quantities of coal products after the war until the 1950s, including urea resin and vinyl acetate resin. In the 1960s, the petrochemical industry began producing epoxy resins, polyurethane resins, acrylic resins, EVA resins and synthetic rubber. Phenol and vinyl acetate also made the switchover to being petroleum-based products; thus, the adhesives industry also transitioned from a coal-based to a petrochemistry-based industry.

Several other fine chemical industries, including the pharmaceutical, pesticide and cosmetic industries, also saw most of their primary raw materials, namely, organic solvents and organic intermediates, switch to petrochemical products.

Thus, in the 1960s, the petrochemical industry became a key industry, supplying a wide range of chemical industries in Japan with their raw materials.

(2) The shift to petrochemistry in chemical industries supplying auxiliary materials to the petrochemical industry

Ammonia, the basic raw material for chemical fertilizers and industrial organic chemicals, was made from hydrogen obtained either from the electrolysis of water, from coke oven gas or from reactions with coke synthesis or water gas. Compared to coal, it was easier to obtain hydrogen from oil, petroleum-based gas and natural gas, since these were hydrocarbons. Moreover, while the large-scale transport of crude oil became possible, rising wages led to an increase in domestic coal prices, meaning that imported oil and petroleum-based gases became cheaper than coal. Furthermore, as the demand for electricity increased, the erstwhile surplus of hydroelectric power soon disappeared. Thus, the 1960s played witness to the ammonia industry switching over from coal to oil and petroleum-based gas. As the size of the ammonia plants grew, they started being built inside petrochemical complexes, where oil and petroleum-based gas were readily available. This was also convenient for acrylonitrile and other petrochemical plants that consumed large quantities of ammonia.

Meanwhile, the world’s caustic soda plants that produced chlorine and sodium hydroxide through the electrolysis of brine were often located in areas where there was a rock-salt layer underground, or where inexpensive power could be obtained by hydroelectricity. Since before the war, most of these plants in Japan had been located in areas that had hydroelectric power plants, using the energy of falling water.

The production of carbide and acetylene was also prevalent in areas where inexpensive power could be obtained, since it consumed large amounts of power. However, an increase in the demand for electricity in Japan during the 1960s saw power generation switch from hydroelectric to thermal power generation using oil. The caustic soda industry had traditionally been driven by a strong demand for caustic soda, while there was little demand for the co-produced chlorine. However, chlorine demand grew rapidly, starting with polyvinyl chlorides in the 1950s. In the 1960s, production skyrocketed of chemical products that used large amounts of chlorine to produce, although the chlorine did not remain in the product, (e.g., propylene oxide, isocyanates and polycarbonate), as did the production of chlorine-based solvents. For this reason, high-capacity caustic soda plants also started being built inside petrochemical complexes. In contrast to their previous inconvenient locations near hydroelectric power, chlorine and other raw materials could now be readily transported to them by pipes, and large amounts of thermal power were being generated nearby. Thus, even the mass production inorganic chemical industries that conventionally had no direct connection to petrochemistry started being located inside petrochemical complexes in greater numbers.

5.5 The 1970s: The end of *Sturm und Drang* for petrochemistry and new challenges

The economic growth experienced in Japan, the United States and Europe during the 1950s and the 1960s ended in the 1970s, and a similar fate befell the petrochemical industry. As polymer-based materials continued to become more commonplace, the period of explosive demand drew to a close. Furthermore, massive crude oil price hikes by OPEC in 1973 and again in 1979 caused the oil crises. The age of cheap crude oil was over. Consequently, the petrochemical industry, which had been using low prices to its advantage, saw its growth restricted from the supply side as well. At the same time, several negative aspects brought about by rapid economic growth manifested in the form of environmental and safety issues, and the petrochemical industry was standing in the firing line. Although new petrochemical technologies were being actively developed until the early 1970s, the pace of development slowed down to such a point in the latter half of the 1970s that many started saying the industry had matured. In addition to this maturation of the technology, petrochemistry also made the jump over to developing countries, thus the trifecta of Japan, the United States and Europe began to collapse.

5.5.1 The end of polymer revolutions in Japan, the United States and Europe

The increase in demand generated by replacing existing chemical industries, such as those based on coal chemistry, with petrochemistry had more or less run its course by the end of the 1960s. In the 1970s, the spread of polymer-based materials in Japan, the United States and Europe had already advanced considerably, thus ending the rapid-growth era for polymer-based materials. Furthermore, the two oil crises caused the price of oil to soar, meaning an increase in both the cost and the price of petrochemical products. This increase in cost relative to other materials was one factor that led to the end of the meteoric growth of petrochemical products.

However, this sea change in the business environment came too quickly for the petrochemical industries in Japan, the United States and Europe to immediately respond. Accordingly, capital investment continued for a little while as it always had, on the back of forecasts for robust demand. Eventually, this led to excess capacity in all three regions. Since facilities had been being upsized from the end of the 1960s onwards, the decline in operating rates led to a dramatic increase in costs, and the profitability of the petrochemical industry suffered as a result.

5.5.2 Manifestation of negative aspects

A lifestyle of mass production, mass consumption and mass disposal spread quickly in the 1950s and the 1960s in step with advancements in petrochemistry. In addition, the pursuit of substantial cost reductions in logistics and other areas propelled the centralization of production, primarily in coastal complexes. However, the effects of these changes were not all positive. Previously unnoticed negative aspects started surfacing in the 1970s; these can be divided into three main issues. The first issue was severe air and water pollution. This was not limited to the petrochemical industry, but rather was an issue shared by all heavy chemical industries. The second issue was plastic waste, which lay squarely with the petrochemical industry. Finally, the third issue was the environmental and safety concerns stemming from chemical substances. Again, this was not limited to the petrochemical industry, but involved a wide range of chemical industries. In the latter half of the 1970s, petrochemical companies in Japan, the United States and Europe were fully immersed in finding solutions to these issues.

(1) Air and water pollution

Air and water pollution were particularly severe issues faced by large complexes in which petrochemical facilities, oil refineries and thermal power generations were concentrated. Complexes regulated concentrations of the air pollutants emitted, such as sulfur dioxide, nitrogen oxide, soot and dust, and water-polluting substances, such as BOD and COD. Regions where emissions were particularly high also made use of total pollution load control schemes. To reduce pollutants, companies converted to low-sulfur fuels, installed flue gas desulfurization equipment, installed dust collectors, modified boiler operating conditions, installed denitration equipment and introduced primary wastewater treatment processes, such as coagulating sedimentation and oil separators, and secondary wastewater treatment processes, such as activated sludge systems. These technologies were applied in every industry, not just the petrochemical industry. Investment in such pollution prevention rapidly increased in the 1970s; in 1975, it accounted for 22% of all investment in the Japanese petrochemical industry.

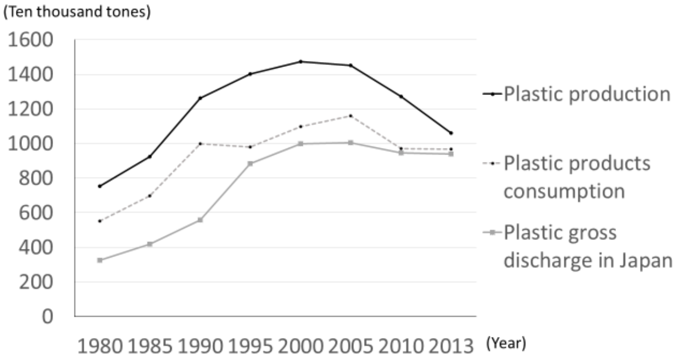
In Japan, measures to mitigate air and water pollution in the petrochemical industry were intensively carried out in the early 1970s, after which the proportion of funds invested in pollution prevention fell away dramatically. Nevertheless, the development of low-pollution production methods that aimed to decrease the amount of byproducts came to form the core of technological development in the petrochemical industry from that time onwards.

(2) Plastic waste

Coinciding with the development of disposable containers, plastic waste became a severe issue for the entire petrochemical industry; the same was true for for old tires as well. However, this problem did not manifest until petrochemical products that were sold and processed were disposed of after being consumed, meaning it could not be solved by the petrochemical industry alone. Since this involved local governments as well as several other related industries and also consumers, measures could not be enacted immediately. In Japan, the Plastic Management Research Association (which was reorganized into the Plastic Waste Management Institute (PWMI) the following year) was established in 1971, and long-term initiatives were commenced with regard to the processing of plastic waste, recycling research, technological development, public relations and the nurturing of a recycling industry.

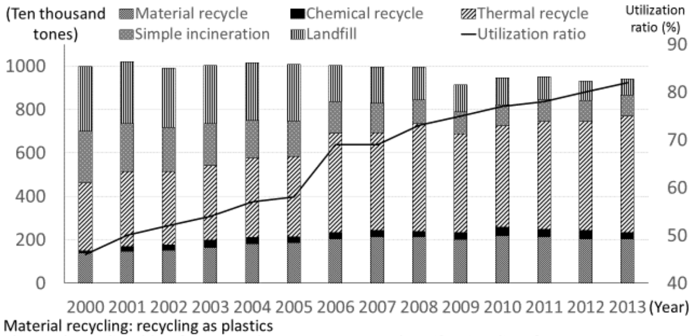
Steady efforts such as these gradually came to produce results in Japan over the next 40 years or so. As Fig. 5.10 shows, the volume of plastic waste continued to increase until it peaked in 2000, and has followed a gradual downward trend since then.

By contrast, the treatment of plastic waste is a different story. In the 1970s, most waste was either buried in landfills or simply incinerated. However, as Fig. 5.11 shows, thermal recycling at municipal waste incinerators had come to be the primary treatment method by the 2000s. Strides were also being made in cooperation with other industries, including the cement and steel industries. In 2000, the utilization rate was 48%; by 2013, this had jumped to 88%. Thus, efforts to tackle the plastic waste problem in Japan are showing signs of success after years of hard work. Notwithstanding, the problem continues to grow across the globe and still remains a major challenge.



Source: Reference [13]

Fig. 5.10 Change in plastic gross discharge in Japan.



Material recycling: recycling as plastics
Chemical recycling: blast furnace, coke oven raw material, gasification, liquefaction
Thermal recycling: solid fuel, waste power generation, heat utilization incineration
Source: Reference [13]

Fig. 5.11 Progress of plastic recycling in Japan.

(3) Environmental and safety issues

stemming from chemical substances

As shown in Table 5.8, four major environmental and safety issues stemming from chemical substances have occurred in the field of petrochemistry, namely, issues with synthetic detergents, issues with organic chlorine compounds, issues with gasoline additives (tetraethyl lead, MTBE) and issues with chemical substances in relation to global environmental problems.

1) Synthetic detergents

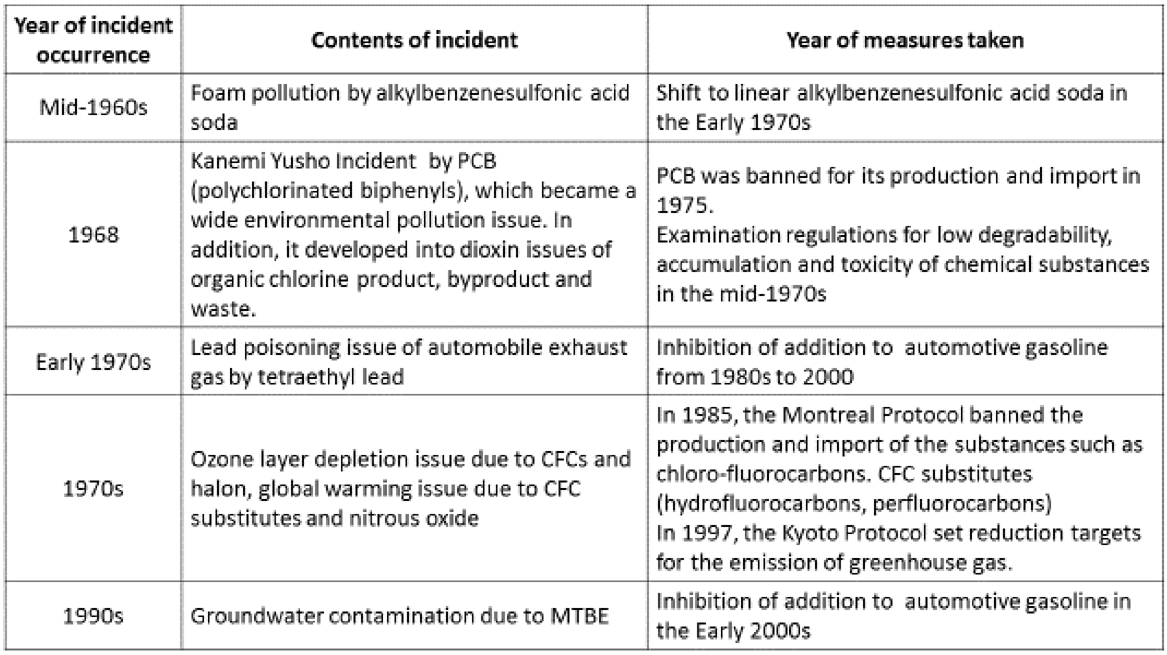
By the mid-1960s, rivers were already starting to become polluted by foam from alkylbenzenesulfonic acid soda, widely used in synthetic detergents. Alkylbenzenesulfonic acid soda used dodecene made from tetramerized propylene as a raw material and possessed strong cleaning power. In Japan, its use as the primary ingredient in synthetic detergent rapidly spread from the late 1950s onwards. However, most of the alkylbenzenesulfonic acid soda derived from dodecene contained branched-chain alkyl groups. Due to its poor biodegradability, the compound remained in the environment and caused foam pollution in rivers. In contrast, the alkylbenzenesulfonic acid soda containing straight-chain alkyl groups were found to be biodegradable. Straight-chain alkyl groups can be obtained from higher alcohols, which themselves are obtained through the high pressure hydrogenation of fats and oils. Consequently, producers switched to using fats and oils to make these. Within petrochemistry as well, various techniques for producing straight-chain α-olefins were developed, thus establishing the infrastructure needed to supply straight-chain alkyl groups. This issue was a major blow to the Japanese and European petrochemical industries, which traced their origins to the steam cracking of naphtha, because it meant the loss of a key consumer for propylene, for which demand was still low. However, manufacturers in both the synthetic detergent and petrochemical industries were quick to respond to this issue.

2) Organic chlorine compounds

In 1968, the Kanemi Yusho Incident occurred in Japan. This was a case of mass polychlorinated biphenyl (PCB) poisoning, but the problem was much bigger, involving dioxins as well as many other chlorinated organic products and their waste products and byproducts. It was then linked to the issue of chlorine-based pesticides, which had been pointed out as problematic in the early 1960s.

PCBs were inexpensive, stable in the presence of heat and chemicals, highly insulating, and highly incombustible, so they were widely used as heat transfer mediums, insulating oils for transformers and capacitors and plasticizers, as well as in carbonless paper. The production of PCBs began in the United States in the late 1920s and in Japan in the mid-1950s. The Kanemi Yusho Incident happened when PCBs, which were being used as a heat transfer medium for the heat treatment of food oil, contaminated food oil due to the inadequate maintenance of a heat exchanger. The production and use of PCBs was prohibited, and PCB-containing products, such as carbonless paper, were widely recalled; however, the problem did not stop there.

Table 5.8 Safety and Environmental issues on chemical substances related to petrochemistry



Year of incident occurrence	Contents of incident	Year of measures taken
Mid-1960s	Foam pollution by alkylbenzenesulfonic acid soda	Shift to linear alkylbenzenesulfonic acid soda in the Early 1970s
1968	Kanemi Yusho Incident by PCB (polychlorinated biphenyls), which became a wide environmental pollution issue. In addition, it developed into dioxin issues of organic chlorine product, byproduct and waste.	PCB was banned for its production and import in 1975. Examination regulations for low degradability, accumulation and toxicity of chemical substances in the mid-1970s
Early 1970s	Lead poisoning issue of automobile exhaust gas by tetraethyl lead	Inhibition of addition to automotive gasoline from 1980s to 2000
1970s	Ozone layer depletion issue due to CFCs and halon, global warming issue due to CFC substitutes and nitrous oxide	In 1985, the Montreal Protocol banned the production and import of the substances such as chloro-fluorocarbons. CFC substitutes (hydrofluorocarbons, perfluorocarbons) In 1997, the Kyoto Protocol set reduction targets for the emission of greenhouse gas.
1990s	Groundwater contamination due to MTBE	Inhibition of addition to automotive gasoline in the Early 2000s

Organic chlorine compounds, like PCBs, do not break down very readily in the environment, and, since they accumulate in body fat, they are perpetuated in high concentrations along the food chain. In the 1960s, it had already been pointed out that chlorine-based pesticides were causing environmental pollution. Furthermore, it was discovered that dioxins, a byproduct generated in the process of producing various organic chlorine products, could potentially contaminate the primary products. Moreover, it was also found that dioxins could be generated when organic chlorine products were incinerated. Like PCBs, dioxins are organic chlorine compounds that are non-degradable, accumulative and toxic.

Efforts were undertaken in Japan, the United States and Europe to tackle this problem, and as a result, management techniques were adopted for all existing and new chemical substances, not just organic chlorine compounds, from the standpoints of degradability, accumulativeness and toxicity. Laws that were enacted in Japan around this time include the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture and the Law concerning Pollutant Release and Transfer Register.

3) Gasoline additives

The third problem was tetraethyl lead. In the late 1960s, questions began to arise surrounding tetraethyl lead, which had been added to gasoline to enhance its octane number. Tetraethyl lead was used in combination with ethylene dibromide to prevent the accumulation of lead oxide in the engine when gasoline was burned. Tetraethyl lead went into commercial production in the United States in the 1920s and was one of the first products of the country’s nascent petrochemical industry. During the Second World War, it was used in large quantities as an octane enhancer for aviation fuel. In Japan as well, it went into commercial production before the war, and was imported *en masse* even after the war since domestic production was not achieved until much later.

Since tetraethyl lead is itself highly toxic, sufficient attention must be given when handling gasoline containing the substance; this had been fully known since the 1920s. In the late 1960s, air pollution caused by lead compounds emitted as automotive exhaust and chronic lead poisoning among roadside residents became significant issues. Therefore, efforts were undertaken to make the switch to unleaded gasoline. Japan had already achieved this transition by the mid-1970s, but in the United States it took until the mid-1990s for leaded gasoline to finally be outlawed. For the petrochemical industry, this meant that demand dissipated for ethylene in the form of tetraethyl lead and ethylene dibromide. To propel the transition to unleaded gasoline, manufacturers either had to produce gasoline containing high quantities of high-octane alkylates or aromatic hydrocarbons or add different additives to gasoline. In the United States, gasoline producers began using MTBE as an additive in the 1980s. MTBE is made by reacting methanol with t-butyl alcohol derived from isobutylene. The production of MTBE increased rapidly in the United States between the 1980s and the 1990s; production in Japan began in 1992. By the end of the 1990s, worldwide MTBE production had reached 18 million tons. With such a large production volume, isobutylene from the steam-cracking of naphtha and FCC waste gas went into short supply. Consequently, half of the required amount of isobutylene had to be produced by dehydrogenating isobutane. Incidentally, MTBE-contaminated groundwater became an issue in the United States in the 2000s. The underlying cause of this was leakage from tiny cracks in underground storage tanks at gasoline stations. MTBE is slightly more soluble than gasoline in water, so it ended up contaminating groundwater. Furthermore, even small amounts of MTBE can dissolve in water, resulting in the water being no longer able to be used for drinking due to the odor and taste. In 2002, the State of California banned the use of MTBE as a gasoline additive, and the remaining states followed suit. By the mid-2000s, petroleum companies stopped adding MTBE to their gasoline. The logical solution would have been to inspect the underground tanks at gasoline stations to prevent leaks, but a government policy was put in place instead, reflecting the growing tendency to regulate chemical substances without much thought. After that, gasoline manufacturers in the United States replaced MTBE with fermentation ethanol. Fermentation ethanol is much more water soluble than MTBE, so the fundamental problem of cracks in underground tanks at gasoline stations has still not been dealt with. As mentioned in Section 4.2.1 (4), the production of fermentation ethanol from corn in the United States skyrocketed between the mid-2000s and the 2010s, reaching 25 million tons of ethylene equivalent. Since corn farmers are subsidized, the use of synthetic ethanol additives made from petrochemicals is prohibited. With this, the petrochemical industry has lost a major consumer of its products, and it has yet to recover. As this shows, the issue of using additives to enhance the octane number of gasoline that started in the 1970s has affected and continues to affect the petrochemical industry in many ways.

4) Chemical substances related to global environmental problems

The fourth category of environmental and safety problems caused by chemicals consists of global environmental problems. This issue began with the ozone layer depletion by fluorocarbons, which contain chlorine and bromine. In the past, fluorocarbons were widely used as refrigerants, safe solvents and propellants. Production in the United States started in the 1930s, while manufacture in Japan began in 1942. Fluorocarbons are produced through a reaction between hydrogen fluoride and chloroform, methyl chloroform and trichloroethylene.

In the mid-1970s, chlorofluorocarbons (CFCs, also known as Freon) and bromofluorocarbons (Halon) were identified as primary causes of ozone layer depletion, and global production and imports of these compounds were banned by the Montreal Protocol in 1985. This resulted in an easing of the ozone depletion trend from the mid-1990s, but no recovery was observed. Hydrofluorocarbons (including hydrogen) and perfluorocarbons (excluding chlorine and bromine) were supplied as new CFC substitutes. However, emissions of these compounds later became subject to restrictions designed to further curb global warming. As a result, it became necessary to develop safer products.

The Kyoto Protocol that was adopted in 1997 for the purpose of reducing global warming set reduction targets for six types of greenhouse gases, including carbon dioxide. In addition to the above-mentioned hydrofluorocarbons and perfluorocarbons, another chemical compound linked to petrochemistry is nitrous oxide (N_2O). Nitrous oxide is a byproduct of the nitric acid oxidation process in the production of adipic acid, a raw material for nylon. The volume of nitrous oxide released in the production of adipic acid was roughly equivalent to 10% of the nitrous oxide produced through human activity; many adipic acid producers have already introduced facilities at their plants to decompose nitrous oxide byproduct.

5.5.3 Maturing petrochemical technology and expansion into developing countries

As illustrated in Table 5.9, the intense technological revolution observed in the 1960s continued in the early 1970s.

Japan commercially manufactured EPDM and IR as new polymers through Ziegler-Natta catalytic reactions, and also introduced the first production of styrene-type thermoplastic elastomers (a major type of thermoplastic elastomers) by leveraging living polymerization. Moreover, the utilization of olefins other than ethylene derived from the steam cracking of naphtha paved the way for the commercial production of acrylic acid ester derived from the direct oxidation of propylene, maleic anhydride made from n-butylene or n-butane feedstock, 1,4-butanediol (PBT resin material) made from butadiene feedstock and THF. The commercial production of high-purity terephthalic acid enabled direct reactions between dimethyl terephthalate (DMT)-independent terephthalic acid and EG, leading to the commercial adoption of manufacturing technologies for polyester filaments (long fibers). This laid the platform to allow polyester fiber to rise far above nylon fiber and acrylic fiber from the 1980s. At the same time, the technology to separate paraxylene, a raw material for terephthalic acid, from mixed xylene was also further developed in the form of Toray's Aromax process and UOP's Parex process, both of which meant substantial cost reductions. The long-desired production alternative to the propylene oxide chlorohydrin method emerged in the form of the styrene co-production method, which was incorporated into commercial production. In Europe and the United States, tert-butyl alcohol and propylene oxide co-production methods were also employed in commercial production on a large scale.

Table 5.9 First production of petrochemical products in Japan in the 1970s

Year	Product	Company, factory
1970	EPDM	Sumitomo Chiba Chemical, Chiba; Nippon EP Rubber, Yokkaichi; Mitsui Petrochemical Industries, Chiba
1970	Acrylic acid ester (direct oxidation of propylene)	Nippon Shokubai, Himeji
1970	Maleic unhydrate (B-Bfraction)	Kasei Mizushima, Mizushima; Nippon Shokubai, Himeji
1970	Styrene-type thermoplastic elastomer	Asahi Kasei, Kawasaki
1971	Isoprene (GPI process), isoprene rubber	Zeon Isoprene, Mizushima
1971	Butanediol, THF co-production (butadiene process)	Toyo Soda Manufacturing, Nanyo
1971	Polyacrylamide	Mitsubishi Chemical Industries, Kurosaki
1972	PBT resin	Mitsubishi Rayon, Toyohashi
1972	High purity telephthalic acid	Matsuyama Sekiyu Kagaku, Matsuyama
1972	Isopropyl alcohol (direct hydration process)	Tokuyama Soda, Tokuyama-higashi
1972	Ethylene-vinyl alcohol copolymer (EVOH)	Kuraray, Okayama
1972	Direct polymerization process for polyester filament	Kanebo Polyester, Hokuriku
1973	PAN process for carbon fiber	Toray Industries, Shiga
1973	Adsorptive separation of p-xylene (Aromax)	Toray Industries, Kawasaki
1975	Styrene monomer, propylene oxide co-production	Nihon Oxirane, Chiba
1976	PET resin for bottles	Toray Industries, Mishima
1977	No decalcification process for polypropylene by the high activity catalyst	Mitsui Petrochemical Industries, Chiba
1978	Superabsorbent polymer	Sanyo Chemical
1978	Ionomer resin	Mitsui Polychemicals, Otake
1979	Modified polyphenylene ether	Asahi Dow, Chiba

Source: Prepared with Reference [10]

From the late 1970s, however, the number of new products and technologies used in commercial production fell rapidly, leading to the view that petrochemical technology had matured. The 1970s saw the establishment of state-operated ethylene production companies first in South Korea and Taiwan, and later in the so-called newly industrialized countries (NICs) (or newly industrialized economies [NIEs]), marking the launch of the petrochemical industry in those countries. Unlike Japan and Europe, these nations had no prior track record in coal-based chemical industry. They used polymers such as polyethylene and polystyrene and synthetic fiber feedstock imported from the three major supply regions, to start production of synthetic fiber as well as molded polymer products. Thanks to the emergence of the textile industry and the household items and home appliance manufacturing sectors, which relied on synthetic fiber and molded polymer products, domestic demand for petrochemical products increased in these countries. Consequently, the relevant governments instituted policies to promote the petrochemical industry with the aim of superceding foreign imports. Since the 1980s, this pattern has governed the rise of the petrochemical industry throughout the ASEAN region, China and India, and it has continued to be repeated to the present day.

As petrochemical technology continued to mature, the driving force behind technology transfer shifted from petrochemical companies developing new technologies to plant engineering companies. As a result, it became easier for state-operated companies and large private companies in developing countries to enter the petrochemical sector. From the 1980s, global demand for petrochemicals fluctuated notably in tandem with an increase in the number of market players.

5.6 Birth of the Middle Eastern petrochemical industry in the 1980s

The event that had the most profound impact on the petrochemical ndustry in the 1980s was the emergence of a large-scale petrochemical industry in the Middle East. This development was symbolic of the maturing state of petrochemical technology and put an end to the dominance of the three major regions that had presided from the 1950s to the 1970s.

At the same time, the petrochemical industry in developed countries witnessed several trends to cope with maturing demand, environmental problems and soaring raw material prices in the 1970s. The first of these trends was the shift toward polymer-based structural materials. Another trend was the development of energy-saving and low-pollution technologies.

5.6.1 Emergence of the petrochemical industry in Middle East

As a result of the steep rise in oil prices during the 1970s, the oil-producing nations of the Middle East had amassed large amounts of capital. Leveraging these funds, the respective governments formulated plans to promote non-oil industries. One such area that was focused on was associated petroleum gas, which had previously been largely neglected. After collection and separation, associated petroleum gas yielded methane (C1), which was used domestically as a fuel and as a raw material for syngas. It also contained ethane (C2), which served as a petrochemical raw material. The remaining propane and butane (C3 and C4, respectively) were exported as LPG, while the condensate was exported as a light petroleum product equivalent to naphtha. While it was possible to also use propane and butane (C3 and C4, respectively) and condensate as petrochemical raw materials, initially only ethane was used as a steam cracking raw material due to problems with long-distance transport. Accordingly, petrochemical production in Middle Eastern oil-producing nations started with a small number of industrial organic chemicals and polymers that were directly derived from ethylene, such as polyethylene, EG, EDC, styrene and synthetic ethanol. The Middle Eastern petrochemical industry was very large in scale, but simple in structure.

The bulk of the petrochemical product manufacturers were joint ventures between state-operated companies in oil-producing nations and European and American oil capital. The technology was entirely supplied by developed nations, with construction subcontracted to plant engineering companies from the West. Middle Eastern oil-producing nations had very little domestic demand for petrochemical products; therefore, virtually all production was geared toward exports. Manufactured products were sold separately by the state-run companies and their European and American capital partners.

As associated petroleum gas had thus far been burned and discarded, these products were supplied to petrochemical producers at exceedingly low (near-zero) costs that were cheaper than energy prices as natural gas. This was one of the reasons why the Middle Eastern petrochemical industry became highly competitive on the global market. That being said, the developed nations tacitly approved such dumping policies as a means to develop new industries in developing nations. The reason for this was that the volume of associated petroleum gas was proportional to the volume of oil production and, in the absence of a sharp increase in the latter, it was believed there would be certain limits on associated petroleum gas volume. Estimates in the 1980s put Saudi Arabia’s production volume of ethylene from ethane included in associated petroleum gas as high as roughly 6 million tons. This was equivalent to roughly 1.5 times the ethylene output of Japan at the time. Based on the prevailing global ethylene demand, it was estimated that this additional supply could be sufficiently absorbed. Existing petrochemical powerhouses such as Europe and Japan were alarmed before Saudi Arabian petrochemical operations began; however, given the concurrent emergence of, and sharp growth in, Asian demand for petrochemical products, the bulk of the exports were redirected to Asia.

In the mid-1980s, the Middle Eastern oil producers began Phase 1 of their Petrochemical Plan, and product sales made steady progress. Around the same time, however, the global supply-demand balance for oil slackened and oil prices declined considerably, resulting in funding issues that delayed the start of Phase 2 of the plan. Thereafter, oil prices resumed an upward trajectory, allowing Middle Eastern oil producers to secure ample funds and reinvest these into large-scale expansion of petrochemical facilities. This pattern has been repeated several times to the present day.

5.6.2 Transition to polymer structural materials

In the 1970s, petrochemical companies in Japan, the United States and Europe faced a maturing demand for petrochemical products, resulting in overcapacity issues. In response, sector players moved away from polymer-based packaging materials and other disposable applications in the 1980s, and instead looked at expanding into applications that could be used over the long term, such as mechanical parts and construction materials. Relative to other materials, plastics offered the benefits of being light and easy to process, and the objective shifted towards maximizing these advantages. The much-anticipated large new market that emerged was the automotive sector. The surge in oil prices at the time had increased demand for fuel-efficient vehicles. One way to improve fuel efficiency was to reduce vehicle weight, and plastics played a role in this respect. Meanwhile, the market for electrical appliances experienced a maturing demand for household appliances as the driving force of growth shifted to electronic products. To meet the needs of both of these markets, plastics required precision molding and heat-resistence.

These new requirements for plastics were met by the field of engineering plastics. Engineering plastics had already been commercially manufactured from the 1950s through the 1960s in the form of polycarbonate, polyamide (nylon), glass fiber filled PET and other compounds, but they had garnered little attention amidst a period of sharp growth in general-purpose resins. From the late 1960s through the 1970s, the so-called general-purpose engineering plastics had made a cursory appearance with the commercial production of polyacetal, PBT and modified-polyphenyleneether. These general-purpose engineering plastics became a springboard for subsequent expansion into the automotive and electronics fields. Thereafter, polymers that undercut engineering plastics on price also came to be used. Some examples include polyurethane, ABS resin, fiberglass reinforced unsaturated polyester and epoxy resin.

As plastics came to be more widely adopted in automobiles, automakers started calling for low-cost plastics. The polymer that addressed those demands was PP. Produced through a block copolymer with ethylene, PP is a plastic that is not only light and easy to process, but also offers superior shock resistance and other mechanical strength properties. Consequently, PP met the needs of the automakers and started gradually replacing the other types of plastic that had originally been introduced in the automotive sector. PP came to account for a dominant share of the plastics used in large molded automotive parts, such as bumpers.

Meanwhile, super engineering plastics such as polyimide, PPS, polyether ether ketone (PEEK) and polyether sulphone (PES) were also successively brought into commercial production in the 1980s, followed by liquid crystal polymers and other plastics. Super engineering plastics were able to withstand temperatures of 150°C and above, which allowed for precision molding and thus paved the way for the further expansion of plastics into the electronics field.

5.6.3 Energy-saving and low-pollution technologies

Following the steep rise in oil prices and the emergence of environmental and safety problems in the 1970s, a number of energy-saving and low-pollution technologies were successively incorporated into commercial production in the 1980s.

(1) Energy-saving technologies

The 1970s had already seen the development of highly active catalysts with HDPE; the technology had progressed to the stage where there was no need to remove the catalyst after polymerization. Consequently, slurry polymerization methods that did not require decalcification and gas-phase polymerization were also adopted in commercial production. Due to its high molecular weight, HDPE facilitated the development of high strength products and production of ultra-thin film with reasonable strength. This enabled resource savings in terms of product usage. The film provided an alternative in fields relying on medium-quality packaging paper, and was widely used in disposable shopping bags and other applications. In the field of synthetic fiber, several energy-saving technologies that shortened production processes were achieved through continuous polymerizing and spinning and high-speed spinning and false twisting (partially oriented yarn - partially textured yarn [POY-PTY]).

The PP highly active catalyst developed by Mitsui Petrochemical Industries (now Mitsui Chemicals) also greatly contributed to energy savings in the 1970s. The prevailing Ziegler-Natta catalyst at the time produced PP with low stereoregularity, which had to be corrected with a solvent. Since large quantities of catalysts were used, decalcification was necessary to subsequently remove catalyst residue from the PP. This made the original PP production process more complex than the method producing HDPE. By contrast, the use of a highly active catalyst yielded little PP with low stereoregularity and also eliminated the need for various catalyst removal tasks because the volume of PP generated was dramatically larger per catalyst volume unit. Further advances in the 1980s led to the commercial production of PP via the gas-phase polymerization method.

A key development in energy-saving petrochemical technology in the 1980s was the commercial production of L-LDPE. As shown in Table 5.10, Japan already used HDPE facilities and commercially produced L-LDPE in 1980, while Union Carbide (UCC) set up a new plant with gas-phase polymerization technology in 1983. Ever since ICI first engaged in commercial production of LDPE in 1930, the polymer had been produced under a high pressure of 2,000 atmospheres and at high temperatures. By contrast, L-LDPE could be produced using medium-to-low-pressure HDPE production technology through the copolymerization of ethylene and lower α-olefins such as 1-butylene (see Section 3.4.2 (1)).

Table 5.10 First production of petrochemical products in Japan in the 1980s

Year	Product	Company, factory
1980	Methanol process for acetic acid	Kyoudo Sakusan, Aboshi
1980 1983	Linear low-density polyethylene by HDPE facility UNIPOL process linear low-density polyethylene	Showa Denko K.K., Oita Nippon Unicar, Kawasaki
1981	Dimethyl ether	Mitsubishi Gas Chemical Company, Niigata
1982	1-Butylene	Nisseki Jushi Kagaku, Kawasaki Mitsui Petrochemical Industries, Chiba
1982	Butane process for maleic anhydride	Nichiyu Kagaku Kogyo, Oita
1983	Polyimide resin	Ube Industries, Ube
1983 1985	Isobutylene direct oxidation process for MMA	Mitsubishi Rayon, Otake Nihon MMA, Ehime
1984	Methacrylonitrile (MAN) process for MMA	Asahi Kasei, Kawasaki
1984	Bio-process for acrylamide	Nitto Chemical Industry, Yokohama
1985	Gas phase process for polypropylene	Sumitomo Chemical, Chiba
1986	PPS	Tosoh (SUSTEEL)
1987	PEEK	Sumitomo Chemical, Chiba

Source: Prepared with Reference [10]

(2) Low-pollution technologies

Low-pollution technologies were successively introduced into commercial production during the 1980s. As already noted, new chlorine-free production methods for propylene oxide were employed in commercial production in the 1970s. There are other petrochemical products that do not contain chlorine in the final product, although chlorine is used in the production process. Chlorine is created through electrolysis and thus requires a heavy energy investment. Since it is ultimately discarded as chlorides, this is a waste of energy. Consequently, proactive research was conducted into chlorine-free production methods in the 1980s. At the time, commercial production of isocyanate had only been partially successful for aliphatic isocyanate. Even today, new production methods for aromatic isocyanate with large output volumes have yet to be adopted commercially. On the polycarbonate front, many production methods were developed that shifted from traditional phosgene and BPA reactions to diphenyl carbonate and BPA reactions; these found their way into commercial production.

In the 1980s, Japanese companies developed several variations on the MMA process and integrated these into commercial production, as shown in Table 5.10. For over 50 years, MMA had been produced through the acetone cyanohydrin process, which utilized a reaction between acetone and hydrogen cyanide. The major drawbacks of this method were the reliance on hydrogen cyanide, a highly poisonous compound, and the generation of byproduct ammonium hydrogen sulfate in volumes that exceeded the resulting MMA by 50%. In contrast, Mitsubishi Gas Chemical developed a ground-breaking process that generated no ammonium hydrogen sulfate even when using the acetone cyanohydrin method, and adopted this into commercial production. Other companies such as Mitsubishi Rayon and Nippon Shokubai developed production methods to manufacture MMA through oxygen oxidation reactions, with isobutylene or tert-butyl alcohol serving as raw materials. These were low-pollution processes that required no use of hydrogen cyanide and did not generate ammonium hydrogen sulfate as a byproduct. They were also effectively leveraged for isobutylene (C4) derived through naphtha steam cracking.

5.7 The 1990s: A shift from petrochemistry to functional chemistry

Global demand for petrochemical products continued to rise, supported by low-cost polyethylene and other products supplied by oil-producing nations. China in particular went through a polymer revolution driven by imported petrochemical products in the 1990s, and started building full-scale petrochemical complexes through joint ventures funded by European and American companies in the 2000s. In the 2010s, the center of global petrochemical demand shifted to Asia. During the same period, the United States underwent a shale gas revolution and moved forward with an ethylene expansion plan targeting a 40%

increase in ethylene capacity from the 2010 level. However, since there is relatively little prospect of growth in domestic demand, this plan has triggered fears of substantial disruption to the global petrochemical supply-demand balance.

As the petrochemical industry in Japan, Europe and the Unites States grappled with a protracted slump, the petrochemical companies in these nations adopted two distinct strategies: the first was to move away from petrochemistry altogether; the other was to keep petrochemistry as the foundation of operations while attempting to migrate to functional chemistry.

Petrochemical technology is generally thought to have matured in the 1970s, but the 1990s witnessed unprecedented new trends that were reflective of changes in the sector's supply-demand environment and other factors.

5.7.1 Emergence of the petrochemical industry in China and the changing face of the Middle Eastern petrochemical industry

The emergence of the petrochemical industry in China followed the same trajectory as it had in South Korea, Taiwan and the ASEAN region. The Chinese polymer revolution started in the 1990s, when petrochemical companies in Middle Eastern oil-producing nations began large-scale exports of low-cost ethylene products. The largest importer of these products was China, which also imported other products that could not be sourced from the Middle East from Japan, South Korea and Taiwan.

The first petrochemical product to be manufactured in China was synthetic fiber, with production volumes increasing up rapidly from the 1990s. To support this effort, several raw materials for synthetic fiber were imported, such as EG, PTA and acrylonitrile. The Chinese textile industry came to dominate the world, firstly in the labor-intensive sewing field, and later in woven, knit and spun materials. Building on its textile industry foundations, China looked to expand into the production of synthetic fiber in the 1990s. Its entry into this market drove a contraction in the corresponding markets in Japan, the United States and Europe. Moving into the 2000s, China rapidly expanded its facilities. This forced countries such as Taiwan and South Korea, which had emerged as synthetic fiber manufacturers in the 1970s, to scale back production. In the 2010s, China's synthetic fiber production grew to account for nearly 70% of the global supply.

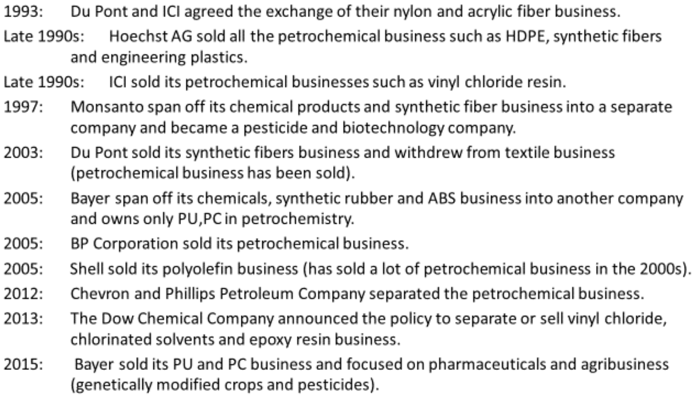
In similar fashion, China's expansion into plastic processed goods also began through the importing of plastics as raw materials. In the 2000s, its imports of petrochemical products ballooned, prompting the construction of large-scale petrochemical complexes centered on naphtha steam cracking in the mid-2000s. These projects were driven by joint ventures with European and American oil and petrochemical companies, which supplied most of the technology. China continued to add new capacity thereafter, but it was unable to immediately replace imports due to the high growth in domestic demand. The expansion has continued since the 2010s, with Asia (including China, South Korea, Taiwan and the ASEAN regions) and the Middle East developing into the largest markets for petrochemical products, both in terms of demand and production volume.

However, the shift of the petrochemical industry to Asia and the Middle East was not necessarily a favorable trend. In several ways, this development significantly skewed the international character of the global petrochemical industry. The first problem is that Chinese and Middle Eastern petrochemical companies have grown into giant organizations that rank among the five top chemical companies in the world. In countries such as South Korea, Taiwan and Singapore, petrochemical companies started out under government control, but were privatized once business took off. Conversely, state-operated companies in the Middle East and China have shown no sign of privatization and have become giant enterprises. Another issue was the absence of international influence in raw material prices. Chinese state-owned petrochemical companies were essentially giant oil refineries, and petrochemistry only accounted for a fraction of their operations. Major oil companies in Europe and the United States withdrew from the petrochemistry business across the board and redirected their attention to their refinery businesses. This left Chinese state-controlled companies as the only players pursuing broad-based petrochemical business, a field in which they gained an alarmingly large presence. Meanwhile, around 2000, repeated rounds of capacity expansion in the Middle East had virtually exhausted the regional supply of ethane derived from associated petroleum gas (APG). Thereafter, local companies were forced to use LPG and condensate, both originally export products, as petrochemical feedstock. However, raw materials prices were set considerably lower than export prices. Since petrochemistry had started out with APG-derived ethane set at a far lower price than the international price, there was no choice but to reduce the price of raw materials for secondary plants relying on LPG and naphtha as feedstock, out of consideration for domestic circumstances. Although the Middle Eastern countries had long since grown beyond the phase of cultivating new industries, their original policies were left unchanged. The petrochemical industry in the oil-producing nations of the region had pursued growth as its primary objective, and as part of this process had gradually broadened its range from an exclusive focus on American-style ethylene products to later also include all Japanese and European olefin-based and aromatic-based products. Faced with poor domestic demand and an inescapable reliance on exports, the Middle Eastern petrochemical industry entered a difficult phase of operations.

5.7.2 European and American oil companies attempt to break away from petrochemistry

The maturing of petrochemical technology that started in the 1970s and the subsequent technology transfer to developing countries led to an emergence of new rivals. Against this backdrop, Japanese, American and European oil petrochemical companies started struggling with chronically excessive capacity and poor earnings. As illustrated in Table 5.11, many of these companies abandoned all future prospects for their petrochemical businesses and exited the petrochemistry field, focusing instead on new growth areas within the chemical sector, such as pharmaceuticals. The transformations were not always successful and several reputable companies, such as Hoechst (Germany) and ICI (United Kingdom), did not survive the process as standalone entities. Others, such as DuPont and Bayer, sold off their petrochemical businesses and looked for new opportunities in the agribusiness and pharmaceutical sectors, but were subsequently unable to regain their former luster. Among the oil giants that had once invested aggressively in the petrochemical field as downstream oil businesses, there was also a growing trend to significantly downsize their petrochemical businesses in tandem with a deterioration in earnings. Meanwhile, investment funds proactively acquired petrochemical businesses and rapidly grew into major global petrochemical enterprises. As petrochemical businesses were being bought and sold based on comparatively short-term outlooks, technology development and other long-term activities lost further steam in Europe and the Unites States.

Table 5.11 Trends of expansion beyond petrochemistry by major Western chemical companies

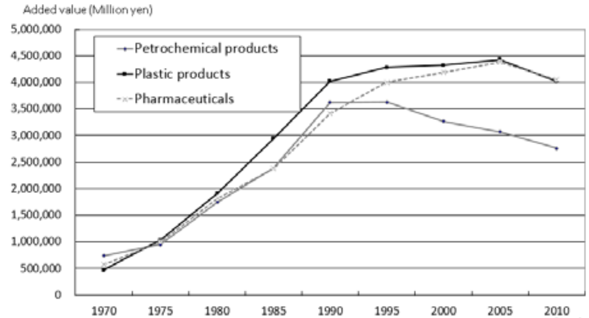


1993:	Du Pont and ICI agreed the exchange of their nylon and acrylic fiber business.
Late 1990s:	Hoechst AG sold all the petrochemical business such as HDPE, synthetic fibers and engineering plastics.
Late 1990s:	ICI sold its petrochemical businesses such as vinyl chloride resin.
1997:	Monsanto span off its chemical products and synthetic fiber business into a separate company and became a pesticide and biotechnology company.
2003:	Du Pont sold its synthetic fibers business and withdrew from textile business (petrochemical business has been sold).
2005:	Bayer span off its chemicals, synthetic rubber and ABS business into another company and owns only PU,PC in petrochemistry.
2005:	BP Corporation sold its petrochemical business.
2005:	Shell sold its polyolefin business (has sold a lot of petrochemical business in the 2000s).
2012:	Chevron and Phillips Petroleum Company separated the petrochemical business.
2013:	The Dow Chemical Company announced the policy to separate or sell vinyl chloride, chlorinated solvents and epoxy resin business.
2015:	Bayer sold its PU and PC business and focused on pharmaceuticals and agribusiness (genetically modified crops and pesticides).

5.7.3 From petrochemistry to functional chemistry

Not all Western petrochemical companies chose to move away from petrochemicals. A large number of companies streamlined their petrochemical businesses to a certain degree, but kept them as the foundation of their operations while pivoting into functional chemistry. BASF and Dow Chemical are typical examples of this. Many Japanese petrochemical companies also followed this path. Examples of success include the world's first commercial production of polyacrylic acid superabsorbent resin by Sanyo Chemical in 1978, and the commercialization of COP for optical resin by Zeon in 1990. The development of such technologies could not have taken place without a foundation in petrochemical technology.

However, functional chemistry extended beyond the scope of conventional petrochemical operations. It entailed not only developing functional polymers, but also concurrent molding technologies, and led to the introduction of functional polymer molded products on the market. This made it more difficult for rivals to enter the sector, and also lifted profitability. Even plant engineering companies with strengths in chemical engineering technology were unable to easily make the leap to molding technologies leveraging the performance of functional polymers. Reflecting this shift toward functional chemistry, the plastics molding industries became the center of Japan's chemical industry in terms of added value. As shown in Fig. 5.12, petrochemistry, plastics molding and pharmaceuticals followed similar growth trajectories as three industries that have supported the Japanese chemical industry from the 1970s to the 1990s. Thereafter, the added value growth in petrochemistry turned from flat to negative, while plastics molding and pharmaceuticals both remained on an uptrend. Rather than the end of growth in petrochemistry, this development should be interpreted as the outcome of an expansion in the scope of business by petrochemical companies to include plastics molding, in order to address new business opportunities. Functional chemistry has since outgrown its traditional classification under petrochemistry, and now also includes polymer molding.



Source: Ministry of Economy, Trade and Industry, industry statistics

Fig. 5.12 Changes in the three largest added values in the Japanese chemical industry.

5.7.4 New trends in petrochemical technologies

Petrochemical technologies are said to have matured in the 1970s. However, the Japanese petrochemical industry continued to incorporate remarkable technologies into commercial production even after the 1990s, as illustrated in Table 5.12. The bulk of these were developed by Japanese chemical companies. Examples in Table 5.12 include cyclohexanol derived from a cyclohexene process, optical resin COP, dimethyl carbonate derived from a low-pressure gas-phase process, MMAs derived from a new acetone cyanohydrin (ACH) process, acetic acid derived from a direct ethane oxidation process, polycarbonates derived from a non-phosgene process, caprolactam derived from an ammonium-sulfate-free co-production process and acrylonitrile derived from a propane method. The Japanese petrochemical industry continues to work on the frontlines of the global development of petrochemical technology today. In addition, the unprecedented technological trends observed in the 1990s increased more and more in the 2000s. In this section, we have only reviewed the circumstances that gave rise to these new technology trends. For details on the technologies in question, refer to Section 6.2.

Table 5.12 First production of petrochemical products in Japan from the 1990s to 2008

Year	Product	Company, factory
1990	Cyclohexanone process for cyclohexanol	Asahi Kasei, Mizushima
1990	Optical resin COP	Zeon Corporation, Mizushika
1992	MTBE	Kashima Oil, Kashima
1992	Low-pressure	Ube Industries, Ube

	gas-phase process for dimethyl carbonate	
1994	PES	Sumitomo Chemical, Ehime
1995	Metallocene gas-phase process for linear low-density polyethylene	Ube Industries, Chiba
1996	New ACH process for MMA	Mitsubishi Gas Chemical Company, Niigata
1997	Ethylene direct oxidation process for acetic acid	Showa Denko K.K., Oita
2002	Non-phosgene process for polycarbonate	Asahi Kasei, Chimei－Asahi Corporation in Taiwan*
2003	Ammonium sulfate-free co-production process for caprolactam	Sumitomo Chemical, Ehime
2004	Metathesis process for propylene	Mitsui Chemicals, Osaka
2007	Propane process for acrylonitrile	Asahi Kasei Chemicals, Tongsuh Petrochemical Corporation in Korea*

Note: The asterisk (*) denotes a technique that a chemical company of Japan has developed, but was produced first at the joint venture overseas.
Source: Prepared with Reference [12]

(1) Technologies aiding the shift from ethylene to propylene

From the 1980s onwards, propylene demand increased steadily on the back of the growth of PP. Around 1970, PP competed with IPA, propylene oxide, acrylonitrile and other compounds, and only accounted for some 15% of propylene demand. By 2010, however, that percentage had increased to over 60%. This shows the remarkably strong growth PP has enjoyed among propylene derivatives. Meanwhile, following commercial production of acetic acid using the methanol process in the late 1970s, the production volume of acetaldehyde dropped considerably from the 1980s, while the demand for ethylene in developed countries declined compared with propylene. Still, petrochemical companies that focused exclusively on ethylene production emerged and expanded in the Middle East, and they flooded global export markets with ethylene products, further narrowing the scope for developed countries to establish naphtha steam cracking plants. Accordingly, propylene shortages became apparent from the 1990s. The price of propylene rose gradually compared with that of ethylene. While it had once hovered at around half of the ethylene price, the price of propylene rose to parity with ethylene by around 2010.

To address these changes in the environment, several new propylene production methods were developed and successively commercialized.

(2) Shift to monomer direct synthesis technology from paraffin

From its onset, petrochemistry has been built on two foundations: olefin chemistry and aromatic chemistry. Saturated hydrocarbons (alkane or paraffin) such as methane, ethane and propane have poor reactivity and extremely limited direct applications. Paraffin is mainly used as a raw material for steam cracking. However, acrylonitrile gave rise to the development of technology to create double-bond industrial organic chemicals from paraffin, and several other potential technologies also came into being as a result. The ongoing development of technologies using paraffin as a raw material could alter the face of traditional petrochemical complexes.

(3) Metallocene and post-metallocene catalysts

The polyolefin field saw the emergence of metallocene catalysts in the 1980s, which attracted attention by virtue of their highly superior performance compared with the traditional Ziegler-Natta catalysts. The new catalysts were first deployed in the field of polyethylene. However, they were unable to exert a profound impact on the petrochemical market in the way the Ziegler-Natta catalysts had in the 1950s and the commercial production of L-LDPE had in the 1980s. Demand for petrochemical products had matured, and minor improvements in productivity and performance proved unable to easily outdo existing product markets. However, this was not the end of the metallocene catalyst technology story. A series of post-metallocene catalysts that surpassed the original metallocene catalysts have been successively announced since the late 1990s.

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6 Technological system and systematization of petrochemistry

We have already outlined the petrochemical products by the number of carbon atoms in Chapter 3, as well as briefly touching on some of the production technologies for each product. In this chapter, we shall discuss the modern petrochemical technology system, taking a cross-sectional view of the technology. We shall also examine new trends in petrochemical technology that have emerged in the 1990s and since, as well as discussing the history of petrochemical technology on the basis of the technology system, examine the essence of petrochemical technology amidst the large number of mass-producing chemical technologies that predated petrochemistry, and introduce epoch-making technologies. Finally, we shall systematize petrochemical technology and discussed its future prospects.

6.1 Technological system and characteristics of petrochemistry

The technological system of petrochemistry as well as the categories of petrochemical products can roughly be classified into three areas: basic petrochemicals, industrial organic chemicals and polymers (Fig. 6.1). A great variety of petrochemical processes are available, because processes developed before the creation of petrochemistry and petroleum refining processes have flowed over into petrochemistry and been developed. This section summarizes the technological system of current petrochemistry.

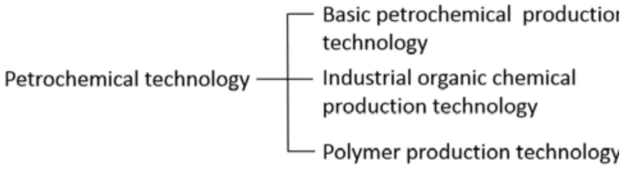


Fig. 6.1 Technology system of petrochemistry.

6.1.1 Technological system of basic petrochemicals

As shown in Fig. 6.2, the technological system of basic petrochemicals from natural gas and petroleum is classified into manufacturing technologies for syngas, olefin and aromatic hydrocarbon.

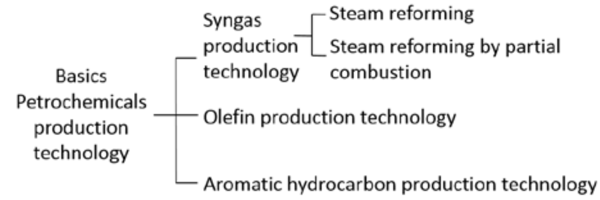


Fig. 6.2 Technology system of basic petrochemicals.

As shown in Fig. 6.3, the manufacturing technologies for olefin are classified into technologies for lower and higher olefins. The former technologies are further classified into technologies for C2 olefin, C3 propylene, C4 butadiene having a conjugated double bond and C4 butylenes having one double bond. Many of these technologies were originally petroleum refining technologies that subsequently flowed over into petrochemistry and were further developed. The latter processes are further classified into technologies for higher linear olefins and branched-chain higher olefins.

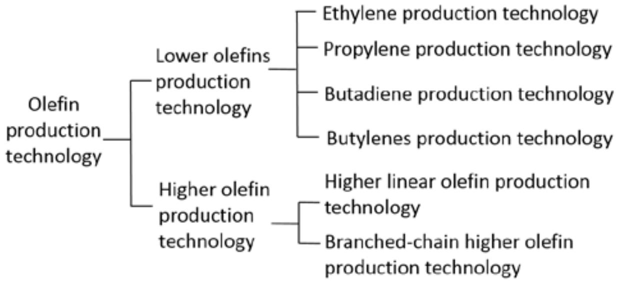


Fig. 6.3 Olefin production technology system.

(1) Ethylene manufacturing technologies

As described in Chapter 4, industrial organic chemicals and polymers were already being manufactured all around the world before the creation of petrochemistry, using raw materials that were available nearby. Figure 6.4 summarizes the technologies for manufacturing ethylene prior to the establishment of petrochemistry. A method of collecting ethylene as a byproduct involved separating ethylene from coke oven gas at low temperature. This method was commonly used in Germany. Another method involved obtaining small quantities of ethylene as a byproduct during the manufacture of acetylene from natural gas using the arc process. Catalytic technologies were also used for the production of ethylene. Ethylene was produced from fermentation ethanol by gas phase dehydration in the presence of acid clay or other catalyst at various places around the world. This technology was essential for early polyethylene production, because it yielded ethylene with higher purity more easily than other technologies. Ethylene was produced by partial hydrogenation of acetylene during the Second World War in Germany. The development of catalysts was the key to the success of this process. Thus, ethylene production technology had its roots in the forests of coal chemistry and even fermentation chemistry.

Meanwhile, ethylene production technology was the first of the lower olefin manufacturing technologies using petroleum as raw materials to be developed, in the form of thermal cracking of heavy oil (Fig 6.5). Heavy oil was thermally cracked to give waste gas containing ethylene and other lower olefins, from which the ethylene and propylene were collected. To obtain gasoline fractions, heavy oil is thermally cracked at high temperature and high pressure in the absence of a catalyst. This is purely a petroleum refining technology. The Burton process developed in 1913 was the first thermal cracking technology for petroleum. It was industrialized by Standard Oil (Indiana) in 1913. The Dubbs process developed in 1914 involved the cracking of petroleum by partial combustion of heavy oil. Subsequently, many petroleum thermal cracking technologies were developed from the 1910s to the 1920s. However, because these were petroleum refining technologies rather than petrochemical technologies to obtain gasoline, they are not detailed here.

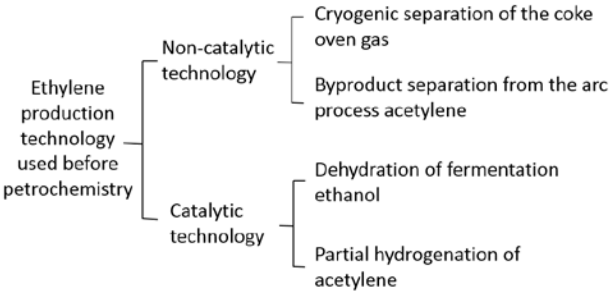


Fig. 6.4 Ethylene production technology predating petrochemistry.

Steam cracking was developed as an extension of thermal cracking of petroleum. This started with the production of ethylene by steam cracking of ethane by U.S. Carbide & Carbon Chemical in 1920. Subsequently, U.S. Standard Oil (NJ) industrialized production of ethylene by steam cracking of propane in the first half of the 1920s and by steam cracking of naphtha in 1941. An outline of steam cracking is given in Section 3.3.3. Steam was added in order to improve the conversion rate by lowering the partial pressure of naphtha or ethane as a raw material to make the thermal cracking equilibrium reaction progress towards the cracking side, to reduce the accumulation of carbon on the internal wall of the reaction tube and to control a thermal cracking-induced temperature fall through the heat of the steam.

As shown in Table 5.3, in addition to tube-type steam cracking that was developed as an extension of thermal cracking of petroleum in the United States, various ethylene manufacturing technologies were suddenly developed and industrialized after the Second World War, competing with each other from the late 1940s to around the 1960s. These technologies included the Catarole process using a copper-iron catalyst (Shell Chemicals 1947), the moving bed cracking process using sand as a medium (TPC process, Socony-Vacuum 1947, sand-cracking process, Lurgi 1955) and high-temperature steam cracking aimed at the co-production of acetylene (BASF process, 1960, Hoechst process, 1960).

Ultimately, only exothermic tube type steam cracking survived the competition in the

1970s. Various exothermic tube type steam cracking processes have been developed, depending on the type of cracking furnace and the method of separating/refining basic petrochemicals, and have been competing with each other. At present, the Stone & Webster process and the Lummus process, among others, are widely used all around the world. Exothermic tube type steam cracking has gone through the following technological developments and improvements. In the first half of the 1960s, the retention time in the tube was shortened from 0.7–1.5 seconds to 0.2–0.4 seconds. This was due to the discovery of the mechanism underlying the adherence of coke to the pipe wall. As a result, the yield of ethylene increased. In the 1960s, the installation of the tube was changed from horizontal to vertical. In the 1960s, a quench heat exchanger (TLE) and a centrifugal compressor were introduced, resulting in energy saving as well as an increase in the size of the equipment.

From the 1950s to the 1960s, of all the olefins made by steam cracking of naphtha, propylene tended to be being produced in excess. Therefore, the triolefin process producing ethylene and n-butylene by disproportionation in the presence of a solid catalyst was developed by Philips in 1960. This process was only industrialized in Canada in 1966. However, because a subsequent expansion in the demand for propylene solved the problem of excessive propylene, the use of this process was discontinued within less than 10 years. Although the mechanism of the reaction was unclear at the time, it was subsequently found to be metathesis reaction via a carbene metal complex. As mentioned in Section 6.2, due to a change in the propylene supply-demand environment, the reverse reaction was revived as a process for manufacturing propylene by the metathesis reaction in the 1990s.

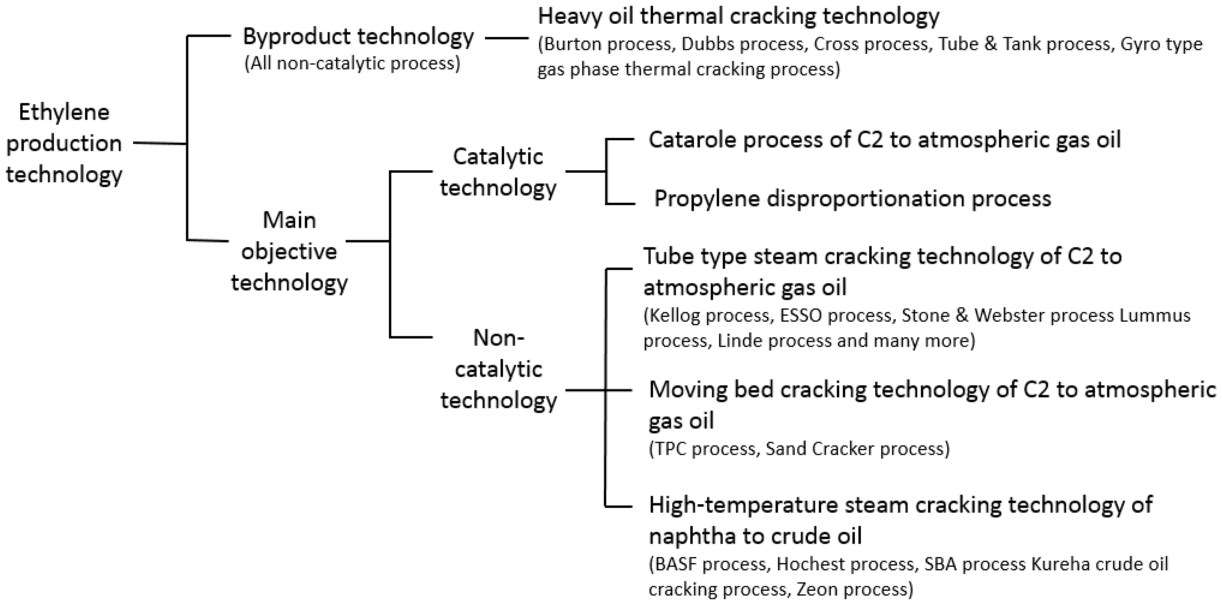


Fig. 6.5 Ethylene production technology system.

(2) Propylene manufacturing technologies

Figure 6.6 summarizes the system of propylene manufacturing technologies. Propylene as well as ethylene is made from waste gas obtained by the thermal cracking of heavy oil. However, petroleum refining technologies to obtain gasoline fractions from heavy oil did not develop towards non-catalytic thermal cracking, but towards catalytic cracking. Houdry (France) developed the fixed-bed cracking process using a silica-alumina catalyst in 1927 and the U.S. Sun Oil industrialized it in 1938. In 1938, Kellogge developed the catalytic cracking process using a fluidized bed catalyst. Standard Oil (NJ) further developed the process by joint studies with Kellogge. It developed the fluidized catalytic cracking

(FCC) process in 1940 and industrialized it in 1942. Meanwhile, Socony-Vacuum developed moving bed TCC as a modification of the Houdry process and industrialized it in 1943.

Waste gas is obtained in larger quantities by the catalytic cracking of heavy oil than by the thermal cracking of heavy oil. Since it contains small amounts of ethylene and large amounts of propylene and butylenes, it became a large-scale supply source of propylene. This is because thermal cracking is a radical reaction, while catalytic cracking is an ionic reaction.

When gaseous raw materials with C3 or C4 and liquid raw materials such as naphtha are steam cracked to obtain ethylene, propylene is also produced in approximately half the amount of ethylene. This process is a major propylene supply source. Especially in Japan, Asia, Europe, etc. where ethylene is produced from naphtha by steam cracking, the steam cracking process is the most important propylene supply source, while waste gas from FCC plants is no more than a secondary supply source and classified as complementary. However, the steam cracking of ethane produces ethylene and only very small quantities of propylene. Therefore, the FCC plants are important propylene supply sources in the United States where ethane is used in larger quantities as a material for ethylene.

Meanwhile, in the 1990s, the supply of propylene from the above two byproduct technologies (steam cracking of naphtha and the FCC process) became insufficient. Therefore, technologies for producing propylene as the main product, such as the reinforced fluidized catalytic cracking process, propane dehydrogenation and the metathesis process, were developed and industrialized. These technologies are described in Section 6.2, “New trends in petrochemical technology.”

Unlike ethylene, propylene has never been synthesized from raw materials other than petroleum to give propylene products since the creation of petrochemistry.

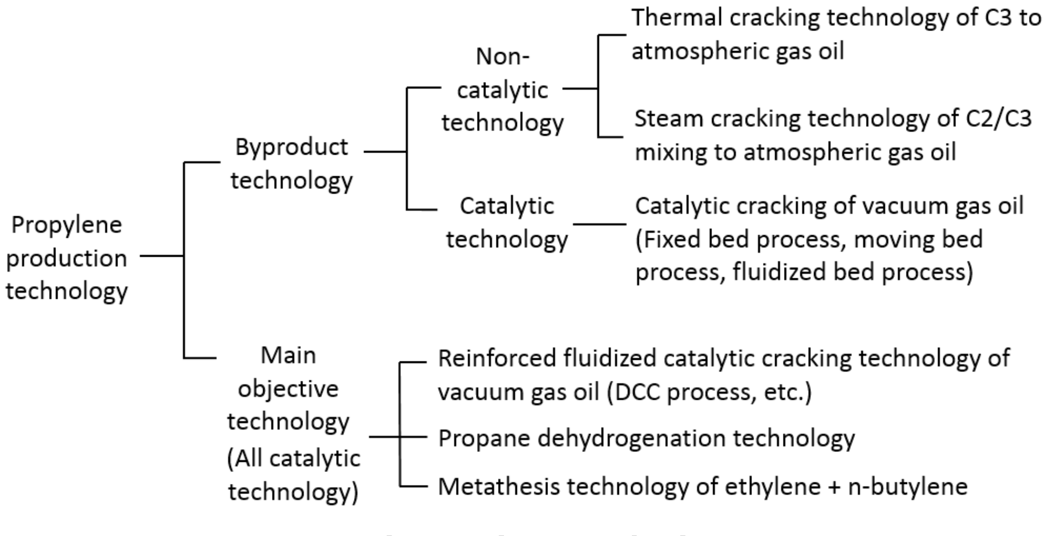


Fig. 6.6 Propylene production technology system.
(No propylene production technology predating petrochemistry)

(3) Butadiene manufacturing technologies

Since the production of synthetic rubber was a very important national issue in Western countries during the Second World War, importance was attached to the production of butadiene. However, because it was not until after the Second World War that steam cracking of naphtha became widely used in Europe and Japan, during the war butadiene was produced in these countries by the processes shown in Fig. 6.7. These were coal chemistry and fermentation chemistry technologies.

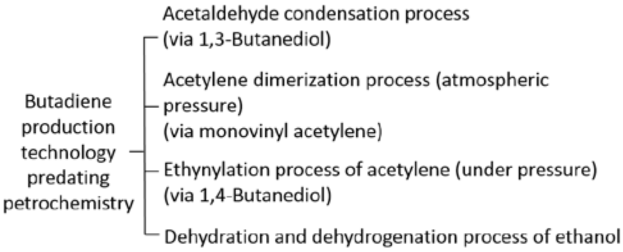


Fig. 6.7 Butadiene production technology predating petrochemistry in Europe and Japan.

The first process is condensation of acetaldehyde. Acetaldehyde was produced from acetylene or fermentation ethanol. Acetaldehyde is condensed and then hydrogenated to give 1,3-butanediol, which is then dehydrated to give butadiene.

The second process is dimerization of acetylene. Under atmospheric pressure, acetylene is dimerized into monovinyl acetylene, which is then hydrogenated to give butadiene.

The third process is ethynylation of acetylene. It is one of the Reppe reactions. Under pressure, acetylene is reacted with formaldehyde to give butadiene via 1,4-butynediol and 1,4-butanediol. However, because the third process was developed at the end of the Second World War, it was only industrialized on a very small scale.

The fourth process is dehydration/dehydrogenation of ethanol. In 1928, it was developed and industrialized in the Soviet Union. During the Second World War, it was also industrialized in the United States. According to a modification of this process, ethanol is oxidized to acetaldehyde, and butadiene is obtained by the dehydration reaction of acetaldehyde with ethanol. This process is described above in Section 5.2.5.

At present, as shown in Fig. 6.8 the most important butadiene supply source is a byproduct of ethylene production by steam cracking of naphtha. However, in this case, a hydrocarbon having more carbon atoms than butane must be used as a raw material, because butadiene cannot be obtained by the steam cracking of ethane or propane.

On the other hand, in the United States where butane and butylene could be obtained in large quantities, the butylene dehydrogenation process shown in Fig. 6.8 was developed and industrialized on a large scale during the Second World War. The raw material for butylene was obtained from waste gas produced from the catalytic cracking of heavy oil. Although this process is not as competitive as the byproduct process from steam cracking, it is still presently used to cover a shortage of butadiene in the United States.

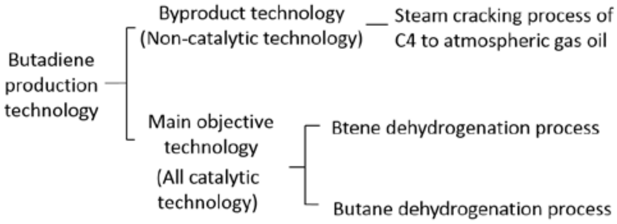


Fig. 6.8 Butadiene production technology system.

Butadiene is also obtained by dehydrogenation of n-butane from waste gas produced by catalytic cracking of heavy oil or natural gas (Houdry process). This process was used during the Second World War, but has not been used since then due to its high cost.

(4) Butylenes manufacturing technologies

As with propylene, butylenes have never produced from raw materials other than petroleum before the creation of petrochemistry. Butylene manufacturing technologies were established only through petrochemistry.

As shown in Fig. 6.9, butylenes are mainly produced from the C4 fraction produced by steam cracking of naphtha or waste gas produced by catalytic cracking of petroleum. Butylenes are obtained as byproducts in both processes. To obtain specific butylenes, Sasol in South Africa separates 1-butylene from synthetic petroleum by the Fisher-Tropsch process. 1-Butylene is used as an ethylene comonomer in manufacture of L-LDPE.

Due to the fact that the demand for butylenes is generally not as strong as that for propylene, processes to produce butylenes as the main product are not widely used. Some examples are as follows. In reinforced fluidized bed catalytic cracking to produce propylene as the main product, butylenes are also produced together with propylene. In Saudi Arabia, 1-butylene is produced by dimerization of ethylene. It is used as an auxiliary raw material for L-LDPE. In Saudi Arabia, n-butylene is produced to obtain propylene by the metathesis reaction of ethylene with n-butylene obtained by dimerization of ethylene. In the 1990s, the demand for MTBE rapidly increased in the United States due to its use as an additive to gasoline. Isobutylene is needed for the production of MTBE. Since isobutylene could not be adequately supplied from the byproducts of steam cracking of naphtha and catalytic cracking of petroleum, it was produced in large quantities by dehydrogenation of isobutane. However, from the 2000s onwards, the addition of MTBE to gasoline was prohibited and as a result, the dehydrogenation of isobutane declined.

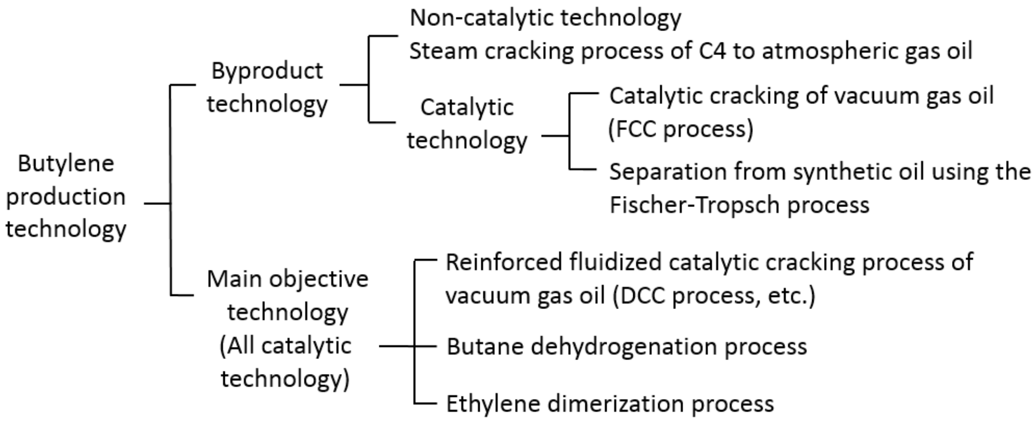
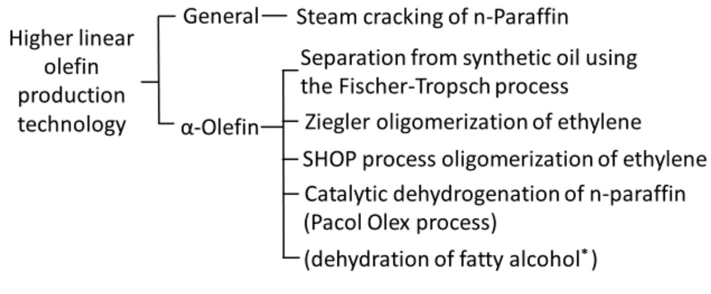


Fig. 6.9 Butylene production technology system.

(5) Higher linear olefin manufacturing technologies Higher linear olefin manufacturing technologies originated in oleochemistry before the dawn of petrochemistry. These technologies are used to produce fatty alcohols by the methyl esterification and high-pressure reduction of fats and oils, and then dehydrate the alcohol to produce α-olefins (Section 4.3.2). Once it became possible to produce alkylbenzenesulfonic acid soda from dodecene by the tetramerization of propylene, it was then possible to produce higher olefins in large quantities. However, this dodecene was often branched rather than linear, resulting in issues of foam pollution (Section 5.5.2 (3) 1). Accordingly, technologies to manufacture higher linear olefins from fats and oils have come to be utilized again.

Meanwhile, several technologies have been developed to produce higher linear olefins using petrochemistry, as shown in Fig. 6.10. Once n-paraffin has been adsorption separated using a zeolite from the kerosene fraction, the n-paraffin can be steam cracked to produce a higher linear olefin mixture with internal or terminal double bonds. Other α-olefin producing technologies include separation from synthetic oil using the Fisher-Tropsch process, Ziegler oligomerization of ethylene, SHOP-method oligomerization of ethylene and catalytic dehydrogenation of n-paraffin.



Note: Fatty alcohols are not petrochemicals, since they are prepared by high-pressure reduction of the methyl esters of fat.
Note: Branched-chain higher olefins production technology: Dimerization to tetramerization of propylenes and butylenes

Fig. 6.10 Higher linear olefins production technology system.

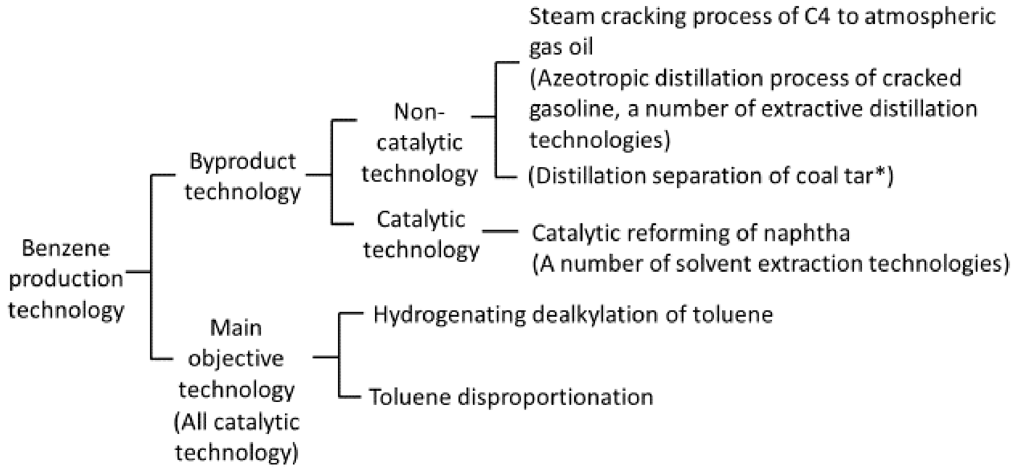
(6) Aromatic hydrocarbon manufacturing technologies

Manufacturing processes for aromatic hydrocarbons as well as those for olefins are very important manufacturing processes for basic petrochemicals. Since before the creation of petrochemistry, benzene, toluene, naphthalene, anthracene, etc. were produced by distillation/separation of coal tar obtained by retorting phase of coal. Even now, this is a significant process for the manufacture of naphthalene. However, it is difficult to obtain xylene from coal tar.

The main supply sources for aromatic hydrocarbons from petroleum are cracked gasoline obtained by steam cracking of naphtha for the production of ethylene and a reformate obtained by catalytic reforming of petroleum for the production of high octane gasoline. Since cracked gasoline contains many aromatic hydrocarbons, benzene can be refined by azeotropic distillation. It is also possible to refine benzene, toluene, etc. after further increasing the concentration of aromatic hydrocarbons by extractive distillation. As the concentration of aromatic hydrocarbon is lower in a reformate than in cracked gasoline, first only the aromatic hydrocarbons are extracted from the reformate by solvent extraction. After extraction, paraffin and cycloparaffin with many branched chains are left in the reformate. These paraffins are useful gasoline ingredients. For solvent extraction, various polar solvents such as ethylene glycols/water, sulfolane, N-methylpyrrolidone/water, Dimethyl sulfoxide (DMSO)/water and N-formylmorpholine/water have been used and many processes such as the Udex process have been developed and industrialized.

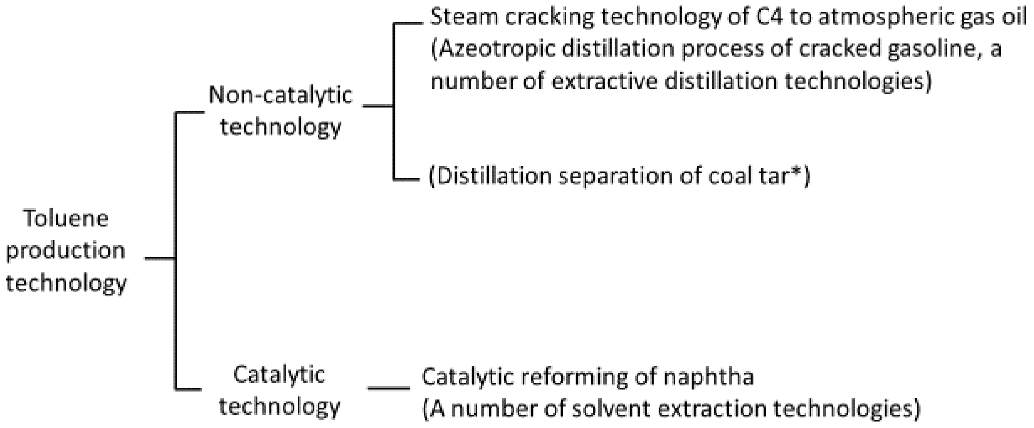
As shown in Fig. 6.11, benzene is refined/separated from the above aromatic hydrocarbon fractions by azeotropic distillation and extractive distillation. Apart from that, hydrogenating dealkylation of toluene and disproportionation of toluene are mainly used for producing benzene. Benzene and methane are obtained using the former reaction, while benzene and xylene are obtained using the latter reaction.

Although toluene is useful as a gasoline fraction, there is little chemical demand for it. Therefore, it is rare for toluene to be obtained from a reformate. It is exclusively obtained from cracked gasoline produced by steam cracking (Fig. 6.12).



Note: Separation by distillation of coal tar is basically not a petrochemical technology, since the raw material is coal. This technology has been used since before the dawn of petrochemistry and is still in use now.

Fig. 6.11 Benzene production technology system.



Note: Separation by distillation of coal tar is basically not a petrochemical technology, since the raw material is coal. This technology has been used since before the dawn of petrochemistry and is still in use now.

Fig. 6.12 Toluene production technology system.

Xylene has three isomers, namely, ortho-, metha- and para-xylenes. Ethylbenzene is also a C8 aromatic hydrocarbon. Since the boiling points of these four aromatic hydrocarbons are similar, it is difficult to separate them by distillation. A mixture of these three xylene isomers, or a mixture of C8 aromatic hydrocarbons with ethylbenzene added, is called mixed xylene. Meanwhile, there is greater demand for o-xylene and p-xylene. Ethylbenzene is used as a raw material for styrene. However, in this case, it is not refined/separated from mixed xylene, because high purity ethylbenzene is synthesized by the reaction of ethylene with benzene.

As shown in Fig. 6.13, mixed xylene is mainly obtained by naphtha steam cracking and reforming. Both processes are byproduct processes. One process that is used primarily for the production of xylene is disproportionation of toluene. Benzene is also produced in this process.

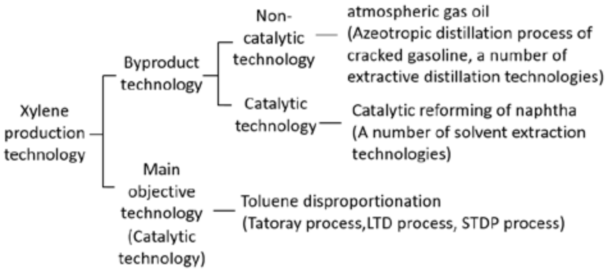


Fig. 6.13 Xylene production technology system.

Crystallization has long been performed for the manufacture of p-xylene, which has the greatest demand (Fig. 6.14). The boiling point of each component of mixed xylene is similar, while the melting point is different, being -95°C, -48°C, -25°C, and 13°C for ethylbenzene, m-xylene, o-xylene and p-xylene, respectively. Consequently, p-xylene can be obtained if mixed xylene is cooled and crystallized. However, the crystallization process consumes much energy. Therefore, once the adsorption process using solid adsorbents such as zeolite and molecular sieves (Aromax process by Toray, Parex process by UOP) was developed, it completely replaced the existing process from the 1970s onwards.

M-xylene has the smallest demand of the three xylene isomers; it is the resulting product once an equilibrium mixture of mixed xylene has been made by isomerization and then o-xylene and p-xylene have been separated from the mixture. As industrial processes, the octafining process (Arco/Engelhard) was developed in the 1960s, followed by the isomer process (UOP), the LTI process (Mobil Chemical), etc. In the 1990s, the HTI process (Mobil), in which ZSM-5 zeolite was partially replaced by platinum, was developed and widely used. This process makes use of the phenomenon whereby the equilibrium reaction is further progressed by the remaining m-xylene and o-xylene because they cannot escape through the empty holes in the zeolite as easily as p-xylene, making the yield of p-xylene higher than the equilibrium concentration.

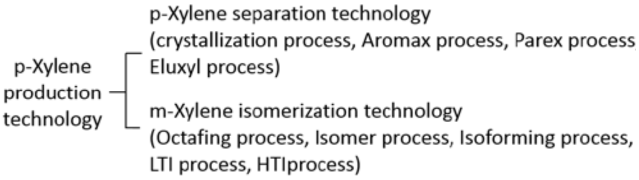


Fig. 6.14 p-Xylene production technology system.

(7) Syngas manufacturing technologies

Syngas was originally manufactured from coke. It was at first manufactured for production of city gas in the latter half of the 19th century and for ammonia, methanol and synthetic petroleum in the first half of the 20th century. It is a very old process. Since it became possible to obtain large amounts of petroleum and natural gas after the Second World War, syngas then began to be manufactured from these materials. As shown in Fig. 6.2, there are two manufacturing technologies. One is exothermic steam reforming in the presence of a nickel catalyst. It is often applied to natural gas. The other is steam reforming by non-catalytic partial combustion. A great variety of raw materials ranging from natural gas to heavy oil can be used.

(8) Summary

The system of technologies for basic petrochemicals has been described for each product in subsections (1) to (7). Further, as shown in Fig. 6.15, these technologies may be cross-sectionally classified into reaction technologies and separation/refining technologies. It is characteristic that the separation/refining technologies are just as significant as the reaction technologies for basic petrochemicals, while the reaction technologies are very significant for the industrial organic chemicals and polymers mentioned below.

In terms of separation/refining technologies, in addition to distillation that is generally performed in chemical technologies, solvent extraction and extractive distillation are performed for the separation of butadiene and aromatics, while adsorption is performed for the separation of n-paraffin and p-xylene. Recrystallization was performed for the separation of p-xylene, but was later replaced by adsorption because it was expensive. Furthermore, in case of difficulty in separation by physical procedures, separation can also be done using differences in reactivity. Some examples are the separation of isobutylene by utilizing differences in hydration reactivity in the presence of a solid acid catalyst and the separation of cyclopentadiene from C5 fraction by using differences in dimerization reactivity.

Meanwhile, the reaction system is broadly classified into non-catalytic and catalytic technologies. Steam cracking as a non-catalytic technologies and catalytic cracking of heavy oil and catalytic reforming of naphtha as catalytic technologies supply far greater amounts of basic petrochemicals. There are many other catalytic technologies, primarily for producing specific basic petrochemicals other than ethylene (propylene by dehydrogenation of propane, butadiene by dehydrogenation of butylene, α-olefin by oligomerization of ethylene, benzene by dealkylation of toluene, benzene and xylene by disproportionation of toluene, p-xylene by isomerization of m-xylene, etc.).

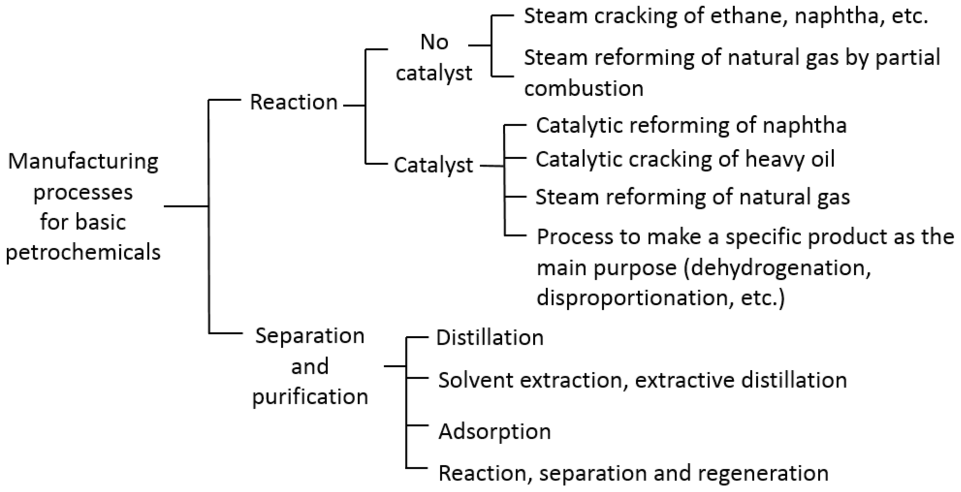


Fig. 6.15 Technology system of basic petrochemicals (summary)

6.1.2 Technological system of industrial organic chemicals

There are a great number of industrial organic chemicals and their intermediates; there are also a great number of processes for manufacturing these products. As shown in Fig. 6.16, the technological system of these chemicals is made up of C1 chemistry [Footnote 1], olefin chemistry, aromatic hydrocarbon chemistry, cycloparaffin chemistry and other synthetic organic chemistry.

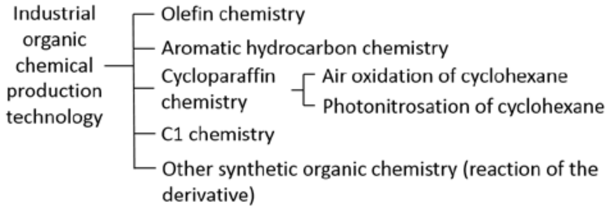


Fig. 6.16 Technology system of industrial organic chemicals.

The reactivity of olefins is not as strong as that of acetylene but not as weak as that of paraffin (alkane). Moreover, olefin chemistry has also developed in many areas due to the fact that not only ethylene but also various other olefins, such as propylene, butylenes and butadiene, are simultaneously produced by the steam cracking of naphtha, one of the olefin manufacturing processes. On this point, olefin chemistry is clearly different from acetylene chemistry, fermentation ethanol chemistry, fermentation acetone/butanol chemistry and other fields that developed before the creation of petrochemistry. Furthermore, there are no derivatives with the potential to progress to the next stage of industrial organic chemicals, like acetaldehyde in acetylene chemistry. In acetylene chemistry, not only C2 products, such as acetic acid, but also various compounds, such as C3 acetone, C4 butyl alcohol and butadiene, were obtained from C2 acetaldehyde. This was because C2 acetylene was the only basic chemical in acetylene chemistry. In petrochemistry, as mentioned in Chapter 3, ethylene oxide, acetone, acrylonitrile, acrolein, phenol, etc. are important derivatives from which further development of various products is expectable, but none of them have as yet grown to a key material comparable to acetaldehyde in acetylene chemistry. In petrochemistry, derivatives with corresponding carbon number atoms are often manufactured from the starting materials of various olefins and aromatic hydrocarbons obtained as basic petrochemicals. Moreover, importance is often attached not to the development of processes for production of expected industrial organic chemicals via several industrial organic chemicals, but to the development of processes that can produce expected industrial organic chemicals from basic petrochemicals, either directly or in as few steps as possible. Furthermore, rather than stoichiometric reactions, petrochemistry often aims at catalytic reactions, using the cheapest

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[Footnote 1] The system of processes for manufacturing C1 or more industrial organic chemicals from C1 methane and syngas and the categories of such products are called C1 chemistry.

possible secondary raw materials, such as oxygen, ammonia or water. In particular, it often aims at reactions that can replace reactions that use elements that are not contained in the final expected product (for example, addition of hypochlorous acid and oxidation by nitric acid). In green chemistry terms, these are reactions with good atom utilization efficiency.

(1) Olefin chemistry: addition to double bonds

As shown in Fig. 6.17, olefin chemistry is classified as addition reactions to the double bond of olefins, reactions to places other than the double bond, and special reactions. Of these, special reactions are further classified into the oxychlorination process and olefin metathesis reactions. Oxychlorination and metathesis reactions are described in (3) of this section and in Section 6.2.1, respectively.

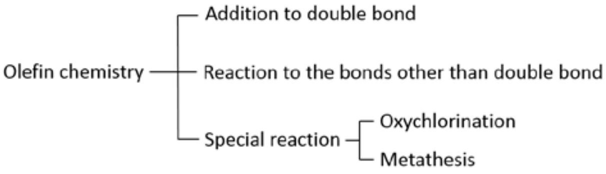


Fig. 6.17 System of olefin chemistry.

The addition reaction to the double bond of olefins is the core of olefin chemistry. It is similar to addition reactions to the triple bond in acetylene chemistry. However, as shown in Fig. 6.18, olefin chemistry is much more diverse than acetylene chemistry.

1) Addition of sulfuric acid, water and alcohol

The addition of sulfuric acid to the double bond of olefins is the oldest petrochemical process. As described in Chapter 5, History of petrochemistry, in 1920, Standard Oil (NJ) produced isopropyl sulfuric acid by the stoichiometric reaction of propylene with sulfuric acid and then hydrolyzed it to make IPA and started industrial production. This process triggered off petrochemistry. Similarly, in 1923, Sharpless Solvent produced amyl alcohol by the reaction of isopentene with sulfuric acid, followed by hydrolysis. In 1930, Carbide & Carbon Chemical produced ethyl sulfuric acid from ethylene and sulfuric acid and then hydrolyzed it to make synthetic ethanol and started industrial production. In the same year, Shell Chemicals started industrial production of sec-butyl alcohol from n-butylene using the sulfuric acid process. However, since production of alcohol by the sulfuric acid process is associated with production of large amounts of dilute sulfuric acid, it must be concentrated for reuse. Consequently, once the catalytic process for directly producing alcohols by adding water (direct hydration) to the double bond of olefins was developed, this method soon replaced the sulfuric acid process. In 1947, Shell Chemicals developed a process for directly synthesizing ethanol from ethylene and steam in the presence of a phosphoric acid catalyst and industrialized it the following year. In 1951, ICI started industrial production of IPA by direct hydration of propylene in the presence of a tungsten oxide-titanium oxide-iron oxide catalyst at 250 atm and 270˚C. Ether is directly manufactured by this process if alcohol is added to the double bond in place of water. This process was used for production of diethyl ether. The MTBE developed in the late 1970s was the first ether to be produced on a large scale. MTBE was produced from isobutylene and methanol in the presence of a solid acid catalyst, such as acid ion exchange resin. At present, ethyl-t-butyl ether (ETBE) is produced from isobutylene and ethanol.

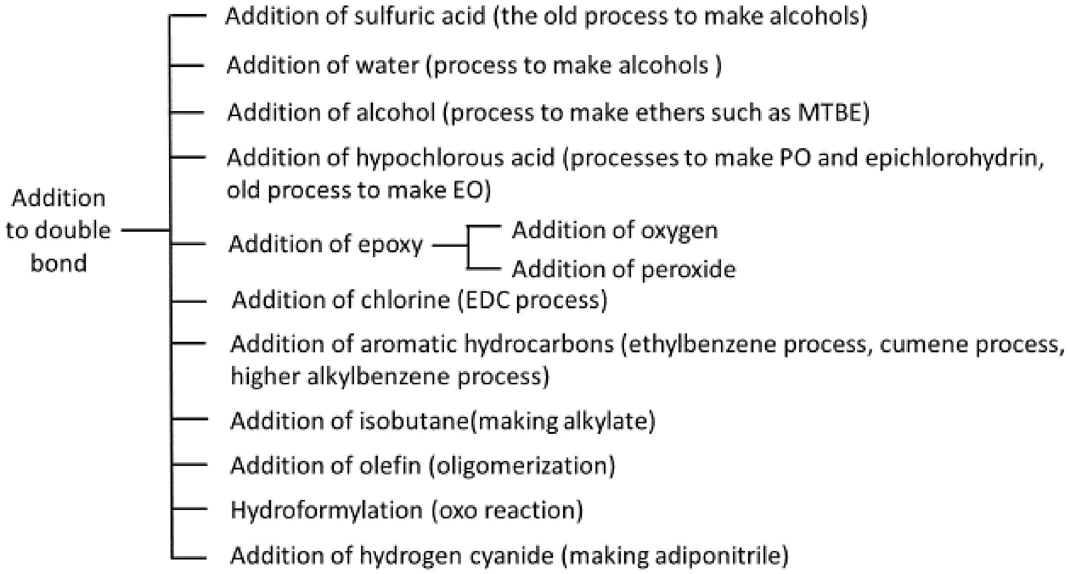


Fig. 6.18 Olefin chemistry; System of technology on addition to double bond.

2) Addition of hypochlorous acid and oxygen

The addition of hypochlorous acid to the double bond of olefins is one of the oldest stoichiometric reactions, along with the addition of sulfuric acid. In 1920, Carbide & Carbon Chemical produced ethylene chlorohydrin by the reaction of ethylene with hypochlorous acid. This process also triggered off petrochemistry. Ethylene oxide is obtained when ethylene chlorohydrin is dehydrochlorinated with sodium hydroxide or calcium hydroxide. Since this reaction is stoichiometric, large amounts of sodium chloride and calcium chloride are produced as byproducts.

Ethylene oxide is reacted with water to give EG, diethylene glycol and triethylene glycol. In the 1930s, ethylene cyanohydrin was made from ethylene oxide and hydrogen cyanide and then thermally cracked to give acrylonitrile. EG can also be made by hydrolysis of ethylene chlorohydrin with sodium hydroxide solution (BASF, 1919).

However, the chlorohydrin process wastes chlorine and sodium hydroxide. In 1937, UCC industrialized a process for directly producing ethylene oxide by epoxidizing ethylene by air oxidation (10–30 atm, 230–325°C) in the presence of a silver catalyst. After the development of this catalytic process, the ethylene chlorohydrin process declined.

It is worth noting that ethylene oxide chemistry developed early in the 1930s because a process was developed for manufacturing ethylene oxide at a low price. In 1937, IG Farben released polyoxyethylene ether of alkyl phenol as a nonionic surfactant. In addition, fatty acid, fatty acid amide and fatty alcohol polyoxyethylene ether were industrialized. In 1944, U.S. company Atlas Powder released an ester of sorbit and fatty acid and its polyoxyethylene compound as nonionic surfactants named Span and Tween, respectively. Ethylene oxide chemistry already started before petrochemistry had fully flourished.

As with ethylene, propylene chlorohydrin is produced by the stoichiometric reaction of propylene with hypochlorous acid and then dehydrogenated with calcium hydroxide to give propylene oxide. In 1929, UCC industrialized this process. However, unlike the case with ethylene, catalytic technologies for directly epoxidizing propylene with oxygen have not yet been developed and therefore, the propylene chlorohydrin process is still used as the main manufacturing process for propylene oxide.

Oxirane Chemical developed the Halcon process in 1968 and industrialized it in 1970. According to this process, a peroxide (hydroperoxide) is made from isobutane, ethylbenzene, cumene, etc. and is then reacted with propylene in the presence of a catalyst to give propylene oxide (see Section 3.4.3 (4)). In the 2000s, it became possible to produce hydrogen peroxide cheaply on a large scale, resulting in the industrialization of a process for producing propylene oxide by the reaction of propylene with hydrogen peroxide. Since only water is produced as a byproduct in this case, the production of propylene oxide is not influenced by the demand for byproducts.

3) Addition of chlorine

The addition of chlorine to the double bond is also an old process. In 1925, Carbide & Carbon Chemical added chlorine to ethylene to give ethylene dichloride (EDC) and started production of it. EDC was dehydrochlorinated to give vinyl chloride. However, in 1932, Griesheim Electron in Germany developed a new process for directly synthesizing vinyl chloride from acetylene and hydrogen chloride in the presence of a mercuric chloride-impregnated silica gel catalyst; as a result, the EDC process was not widely used for the production of vinyl chloride.

After the Second World War, as ethylene became supplied cheaply in large quantities by steam cracking, the EDC process revived. Initially, the dehydrochlorination reaction to produce vinyl chloride from EDC was a liquid-phase stoichiometric reaction using an alkaline solution. However, in this case, half of the chlorine was wasted as alkali salt. After that, gas phase cracking in the presence of a pumice stone or activated charcoal catalyst was developed. In this case, half of the chlorine could be collected as hydrogen chloride. However, this had the disadvantage in that the life time of each catalyst was short; as a result, the noncatalytic thermal cracking process was widely used, in which EDC was passed at high speed through a high temperature and pressure pipe. Since the EDC was thermally cracked to give vinyl chloride and equimolar hydrogen chloride, the combined ethylene-acetylene process was developed for producing vinyl chloride by the reaction of hydrogen chloride thus obtained with acetylene. However, after the ethylene oxychlorination process was developed in 1965, the acetylene process and the combined acetylene-ethylene process both declined rapidly, while the combined EDC-oxychlorination process became exclusively used (see Section 5.4.2 (2) 4)). According to the ethylene oxychlorination process, ethylene, hydrogen chloride and oxygen (or air) are reacted to give EDC in the presence of a copper chloride/potassium chloride catalyst. The key point of this process is that hydrogen chloride obtained as a byproduct of thermal cracking of EDC is reacted with ethylene to give EDC.

The development of industrial processes for manufacturing chlorine from hydrogen chloride started a long time ago. In the 1820s, the Leblanc process as the first method of manufacturing soda (patented in 1791 in France) was actively used in the United Kingdom. However, the hydrogen chloride byproduct of this process was released into the air and rivers, leading to the enactment of the Alkali Act in the United Kingdom in 1863. Investigations were conducted to collect hydrogen chloride and make it into chlorine and then into bleaching powder. As a result, the Weldon process (a liquid-phase process using a manganese dioxide catalyst) and the Deacon process (a gas phase process using a cuprous chloride-impregnated brick catalyst, the world’s first heterogeneous gas phase process) were developed in 1866 and 1868, respectively. Since the Weldon process produced thick gas, it was industrialized immediately. Meanwhile, since the Deacon process produced dilute gas, it was not until the 1880s that the process came into wide use, after Hurter conducted fundamental studies on the absorption of hydrogen chloride. In 1932, Raschig developed an oxychlorination process for producing chlorobenzene from benzene, hydrogen chloride and oxygen in the presence of a copper oxide-cobalt oxide-alumina catalyst or a copper oxide-iron oxide-alumina catalyst. This process was an important constituent of the Raschig process (formation of phenol and hydrogen chloride from chlorobenzene and water) by gas phase hydrolysis of chlorobenzene, industrialized in 1935 (see Section 4.6.1). This Raschig process became a model for the ethylene oxychlorination process.

A process in which hydrogen chloride as a byproduct of thermal cracking of EDC was made into chlorine using a method similar to the Deacon process and reused was also developed and industrialized. However, the EDC production process by reproduction of chlorine was short-lived. This was because the ethylene oxychlorination process was industrialized immediately after the development of this process. Chlorine is not produced by the ethylene oxychlorination process, because ethylene is chlorinated in the presence of a copper oxide catalyst and the reduced catalyst is reproduced by air and hydrogen chloride.

The application of the oxychlorination process has not yet been extended to compounds other than EDC and chlorobenzene. In 1975, a process for manufacturing chloromethane from methane, hydrogen chloride and oxygen in the presence of a copper chloride/potassium chloride fused salt catalyst was industrialized. However, this process did not create any major applications for oxychlorination.

4) Addition of aromatic hydrocarbon, isobutane and olefins

The addition of aromatic hydrocarbons [Footnote 2], isobutane and olefins to double bonds is a petroleum refining technology that developed in the 1930s. Petroleum waste gas containing olefins is reacted with benzene in the presence of an aluminum chloride catalyst to give ethylbenzene and cumene. Polymer gasoline is obtained by dimerization or trimerization of olefins in the presence of a phosphoric acid catalyst, while alkylate gasoline is obtained by the reaction of olefins with isobutane.

Of these compounds, ethylbenzene and cumene obtained by the addition reaction of aromatic hydrocarbons to double bonds are important raw materials for petrochemical products. Ethylbenzene is dehydrogenated to give styrene. In 1930, styrene was industrialized by IG Farben. Ethylbenzene was produced by the liquid-phase process in the presence of an aluminum chloride catalyst [Footnote 3]. In 1953, Koppers Chemical started production of ethylbenzene using the gas phase process in the presence of a phosphoric acid-silica/alumina catalyst. In 1958, UOP developed a gas phase process using a boron trifluoride-hydrogen fluoride catalyst. This was followed by the development and industrialization of the Mobil-Badger process, which uses a zeolite ZSM-5 catalyst, in 1980. It was subsequently widely used around the world. To improve manufacturing processes for ethylbenzene, attempts have been made to control higher order alkylated substances, to improve the conversion rate, to decrease the corrosiveness of catalysts and to prolong the life time of catalysts.

Benzene is added to the double-bond of propylene to give cumene. Cumene is exclusively used for the production of phenol and acetone by the oxidation/cleavage reaction. This phenol/acetone co-production process using the cumene process was developed by Hock and Lang in 1944 and was then industrialized by Hercules (United States) and Distillers (United Kingdom) in 1953. Cumene is synthesized in the presence of a sulfuric acid/aluminum chloride/hydrogen fluoride catalyst in the liquid-phase process, while it is synthesized by addition of steam in the presence of a phosphoric acid-silica catalyst in the gas phase process. Subsequent improvement of catalysts resulted in the use of a zeolite catalyst, as was used for ethylbenzene. Use of the zeolite catalyst has spread rapidly since its industrialization in 1996.

The third most important addition reaction of aromatic hydrocarbons to the double bond of olefins is the production of higher alkylbenzene from higher olefins and benzene. The sulfonate of higher alkylbenzene is an important anionic surfactant and is used in large quantities for detergents. The addition of benzene to higher olefins is often performed by liquid-phase process in the presence of hydrogen fluoride, aluminum chloride, etc. as a catalyst.

5) Hydroformylation (oxo process)

[Footnote 2] This reaction is usually classified as an alkyl-group substituention reaction into aromatic hydrocarbons (alkylation). However, it is described here, because it can formally be considered an aromatic hydrocarbon addition reactionfrom the olefin perspective.

[Footnote 3] Ethyl chloride that is made by the reaction of fermentation ethanol with hydrogen chloride is reacted with benzene in the presence of an aluminum chloride catalyst to give ethylbenzene without going through ethylene. This route was selected in countries where fermentation ethanol could be obtained more easily than ethylene. This is a typical Friedel-Crafts reaction.

In the hydroformylation of olefins, hydrogen and a formyl group (-CHO) are added to the double bond to give aldehyde with one more carbon atom than the original olefin. Aldehyde is made into various derivatives by reduction (alcohol), oxidation (carboxylic acid) and aldol condensation. In 1938, Roelen (Ruhr-Chemie) discovered that propionaldehyde is produced when ethylene is reacted with carbon monoxide and hydrogen in the presence of a cobalt catalyst ($HCo(CO)_4$). When propylene is reacted in the above manner, the main product is n-butyraldehyde, although isobutyraldehyde is also obtained. n-butyraldehyde is hydrogenated as it is to give n-butanol, or hydrogenated after aldol condensation to give 2-ethylhexanol. These alcohols were reacted with phthalic anhydride to give phthalate esters, which were used as plasticizers for polyvinyl chloride. Since 2-ethylhexanol in particular is used in large quantities even now, n-butyraldehyde is in great demand, although there is an excess of isobutyraldehyde.

In 1975, UCC and other companies succeeded in the industrialization of the hydroformylation process using the Wilkinson catalyst (triphenyl phosphine-coordinated rhodium catalyst). This process can makes a significantly higher n-aldehyde/isoaldehyde ratio than the cobalt catalyst process. Hydroformylation is applied not only to ethylene and propylene, but also to C7–C12 olefin oligomers, such as isoheptene, diisobutylene and tripropylene. C8–C13 oxoalcohols produced by this reaction are made into phthalate esters and then used as plasticizers. C11–C18 α-olefins undergo hydroformylation to give C12–C19 linear higher alcohols. These are used for the production of surfactants and fiber auxiliaries.

6) Addition of hydrogen cyanide

The addition reaction of hydrogen cyanide to double bonds is important for the production of adiponitrile in petrochemistry. Among several presently available methods of manufacturing adiponitrile, the most common is the addition of two hydrogen cyanide molecules in two stages to butadiene in the presence of a nickel-triallyl phosphite catalyst. Adiponitrile is hydrogen reduced to give hexamethylenediamine, which is then used as a raw material for 6,6-nylon.

(2) Olefin chemistry: Reaction to places other than double bonds

Like ethynylation (reaction acetylene of to hydrogen) as one of the Reppe reactions in acetylene chemistry, the reaction to hydrogen adjacent to the double bond and the reaction to hydrogen in the methyl group adjacent to the double bond (hydrogen at the allylic position) were successively developed in olefin chemistry from the latter half of the 1950s onwards (Fig. 6.19). As a result, the demand for olefin chemistry using propylene and butylene as starting materials expanded dramatically, despite it once having a lower demand than ethylene.

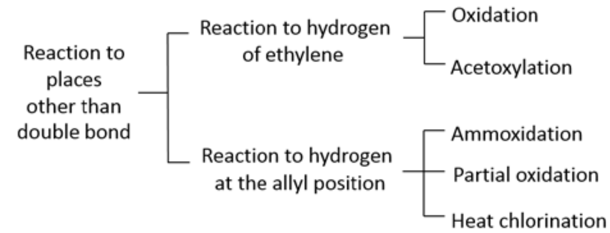


Fig. 6.19 Olefin chemistry; System of reactions to places other than double bonds.

1) Direct synthesis of acetaldehyde from ethylene

In acetylene chemistry, acetaldehyde was made by the addition of water to acetylene, from which important derivatives such as acetic acid, acetone and butadiene were produced. However, the process for producing acetaldehyde from ethylene is time-consuming, because ethanol must be synthesized first and then oxidized to give acetaldehyde. In 1930, UCC industrialized this process using ethylene from petroleum waste gas as a raw material; many U.S. chemical companies later produced acetaldehyde by this process.

In 1894, F.C.Phillips found out that ethylene was stoichiometrically oxidized by palladium metal salt to give acetaldehyde. This reaction is very unique in that hydrogen of ethylene is replaced by the palladium metal salt hydroxy group derived from water. The resulting vinyl alcohol becomes acetaldehyde as a tautomer. More than 60 years later, this reaction was converted to a catalytic reaction and used as a petrochemical process. In 1956, Schimidt (Wacker Chemie) discovered a reaction to synthesize acetaldehyde from ethylene and oxygen in the presence of a redox catalyst that was an aqueous solution of copper chloride containing a small amount of palladium chloride [Footnote 4]. In 1959, Wacker Chemical, jointly with Hoechst, completed an industrial process using this reaction. In the one-stage process (Hoechst process), the oxidation of ethylene and reproduction of palladium salt take place at the same time in the same reactor. Since the conversion rate of ethylene is 35–45% under conditions of 3 atm, 120–130°C and liquid-phase reaction, it requires the circulation of unreacted gas. Therefore, highly purified ethylene and oxygen are used. In contrast, in the two-stage process (Wacker process), oxidation of ethylene and reproduction of palladium are performed separately. As the conversion rate of ethylene is nearly 100% under conditions of 10–12 atm, 100°C and liquid-phase reaction, circulation of unreacted gas is not needed and reproduction of palladium can be performed with air. The idea of the redox catalyst as an aqueous copper solution containing palladium chloride was truly epoch-making.

As mentioned in Section 5.3.2 (3), one of the two core products in acetylene chemistry (acetaldehyde and vinyl chloride) declined due to the development of this reaction early in the 1960s. This prompted rapid progress in petrochemistry.

2) Acetoxylation of ethylene

When ethylene and air are passed through an acetic acid solution in the presence of sodium acetate using a palladium chloride-cupric chloride solution catalyst, acetoxylation of ethylene occurs to give vinyl acetate. In the 1960s, ICI and Celanese industrialized this process by liquid-phase reaction. However, both companies discontinued it within a few years, because corrosion occurred. Bayer and Hoechst succeeded in the industrialization of this process by gas phase reaction in the presence of a solid catalyst composed of silica-impregnated palladium salt. This process also replaced the method of manufacturing vinyl acetate from acetylene and acetic acid.

3) Ammoxidation of propylene

In the 1930s, the demand for acrylonitrile as a raw material for synthetic rubber (NBR) expanded; as a result, an ethylene cyanohydrin process was developed using the stoichiometric reaction of ethylene oxide with hydrogen cyanide, and production of acrylonitrile started. Around the 1950s, production of acrylic fiber also started in the United States, resulting in a rapid increase in the demand for acrylonitrile. To increase the supply, American Cyanamid developed a process for adding hydrogen cyanide to acetylene and industrialized it in 1955. In 1957, Knapsack-Griesheim developed a process for manufacturing acrylonitrile, in which lactonitrile made by the reaction of acetaldehyde with hydrogen cyanide was dehydrated to give acrylonitrile. Due to the fact that a process for directly synthesizing acetaldehyde from ethylene (Hoechst-Wacker process mentioned above) was developed simultaneously, acrylonitrile production was expected to become a large-scale consumer of acetaldehyde.

However, in 1958, the U.S. Sohio developed a propylene ammoxidation process. According to this process, propylene, ammonia and air are reacted in the presence of a bismuth molybdate catalyst in a fluidized bed at 450˚C. At almost the same time, Distillers (the United Kingdom) also developed a manufacturing process using a bismuth molybdate catalyst. In the ammoxidation of propylene, it is the methyl group (hydrogen at the allylic position) rather than the double bond of propylene that reacts to give a nitrile group. This was quite an epoch-making reaction that had previously been unknown. The development of this process meant a decline in the hydrogen cyanide addition process using acetylene as a raw material as well as the acetaldehyde process using ethylene as a raw material, and propylene became a raw material for acrylonitrile.

[Footnote 4] The mechanism of this reaction has been investigated in detail, showing that the oxygen of acetaldehyde is not from air, but from water used as a solvent.

Catalysts for ammoxidation were subsequently improved by the addition of various promoters to bismuth-molybdenum complex oxides. In addition, various industrial catalysts were developed, such as a bismuthic acid-uranium catalyst containing depleted uranium. In the Sohio process, the yield of acrylonitrile was initially not so high due to the production of hydrogen cyanide, acetonitrile and other byproducts. Catalysts have subsequently continuously been improved to increase the yield of acrylonitrile and to decrease the formation of byproducts.

4) Partial oxidation of the methyl group adjacent to the double bond of olefins

Following the ammoxidation process, production of acrolein by partial oxidation of the methyl group of propylene to aldehyde was industrialized using a bismuth molybdate or bismuth phosphomolybdate catalyst that was also used for acrylonitrile. Acrolein is further oxidized to give acrylic acid, which is then esterified to give acrylic acid esters. Acrolein was also used as a starting material for synthetic glycerin.

Production of acrolein began with the industrialization of a gas phase condensation reaction of acetaldehyde with formaldehyde by Degussa in the early 1940s, in the period of coal chemistry. In 1958, Shell Chemical industrialized a process for manufacturing acrolein by the oxidation of propylene in the presence of a cuprous oxide catalyst, while Distillers developed a propylene oxidation process using a copper oxide-silica catalyst. However, once the above bismuth molybdate catalyst was developed, it was the main process used.

When n-butylene is air oxidized in the presence of a vanadium oxide catalyst, both of the methyl groups are oxidized to give maleic anhydride and maleic acid. In 1962, the U.S. Petro-Tex Chem industrialized this process. In 1970, Mitsubishi Chemical industrialized a fluidized bed process using a vanadium pentoxide-phosphoric acid catalyst. This method was outstanding in terms of heat removal.

The method of manufacturing MMA from isobutylene developed by many Japanese companies is a significant, world-first process. Only one of the methyl groups of isobutylene is oxidized. In 1982, Nippon Shokubai became the first in the world to industrialize it. The following year, Mitsubishi Rayon also industrialized it using its own technology. Isobutylene is at first made into t-butyl alcohol in the presence of an acid catalyst, such as ion exchange resin, and then into methacrolein by oxygen oxidation/dehydration in the presence of a molybdenum/iron/nickel-based catalyst. Therefore, while the double bond of isobutylene is retained, the methyl group is not necessarily partially oxidized. A heteropolyacid catalyst is used for oxygen oxidation of methacrolein into methacrylic acid.

MMA has been produced by the acetone cyanohydrin process, in which acetone is stoichiometrically reacted with hydrogen cyanide, since the 1930s. The isobutylene process developed by several Japanese companies is now replacing the acetone cyanohydrin process all around the world.

5) Chlorination of propylene at the allylic position

While the addition of chlorine to propylene is easy, the resulting dichloropropane is not industrially important, unlike EDC, because it is not in demand. On the other hand, at 300°C or higher, substitution reaction of chlorine to hydrogen at the allylic position of propylene occurs in place of addition reaction. By using this reaction, Shell Chemical developed a method of manufacturing allyl chloride in 1937 (see Section 3.4.3 (9)).

(3) Aromatic hydrocarbon chemistry

In the middle of the 19th century, aromatic hydrocarbon chemistry bore fruit in the synthetic dye industry using coal tar as a raw material. In particular, substitution reactions of aromatic rings, such as chlorination (e.g. chlorobenzene), nitration (nitrobenzene) and sulfonation (benzenesulfonic acid), and reactions of their functional groups to introduce various substituents, such as amine (aniline), diazo and hydroxyl (phenol) groups, were almost all completed in the latter half of the 19th century. Furthermore, the chlorination of side-chain methyl groups, the synthesis of derivatives of the resulting chlorinated substances, such as benzyl alcohol and benzoic acid, and the production of phthalic anhydride, maleic anhydride, etc. by partial oxidation of naphthalene and benzene rings were also completed under the umbrella of aromatic hydrocarbon chemistry before the creation of petrochemistry. In 1941, IG Farben started production of polyurethane foam composed of TDI. In 1958, DuPont started production of MDI. TDI and MDI were manufactured by the process for synthesizing aromatic isocyanate using the reaction of aromatic amine with phosgene.

As mentioned above, the technological system of large-scale aromatic industrial organic chemicals was already nearly completed under coal tar chemistry. Meanwhile, dehydroalkylation of toluene, disproportionation of toluene, isomerization of xylene, alkylation of aromatic hydrocarbons, etc. were developed in petroleum refining chemistry in the 1930s.

Aromatic hydrocarbon chemistry, which developed in the fields of coal tar chemistry and petroleum refining chemistry flowed over into petrochemistry. Accordingly, as shown in Fig. 6.20, the direct oxidation of side chain methyl groups and the oxidation of hydrogen at the α-position of side chain alkyl groups are the only processes of aromatic hydrocarbon chemistry that were developed as new petrochemical processes after petrochemistry began to fully develop in the 1950s.

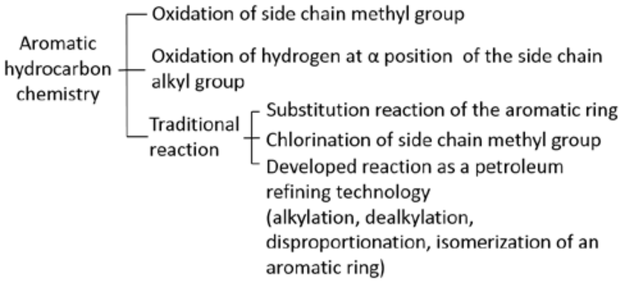


Fig. 6.20 System of of aromatic hydrocarbon chemistry.

1) Direct oxidation of side chain methyl groups

In 1969, BASF developed a process for manufacturing phthalic anhydride by air oxidation of o-xylene in the presence of a vanadium oxide-based catalyst. In coal tar chemistry, a method of manufacturing phthalic anhydride from naphthalene by air oxidation of naphthalene in the presence of a vanadium oxide-based catalyst had been industrialized in 1916 (see Section 4.6.2). Therefore, it may be said that air oxidation of o-xylene was developed as an extension of coal tar chemistry.

Meanwhile, terephthalic acid as a raw material for polyester developed together with petrochemistry, since production of polyester started around 1950. In air oxidation of p-xylene, one of the two methyl groups can be oxidized to give paratoluic acid, but the second methyl group cannot be oxidized as readily as in o-xylene. In 1951, DuPont industrialized a stoichiometric process for oxidizing p-xylene with nitric acid in two stages, and started producing terephthalic acid. Oxidation with nitric acid is more costly than air oxidation and oxygen oxidation. Subsequently, aiming at cost reduction, ICI developed a manufacturing process in which air oxidation and nitric acid oxidation were performed in the first and second stages, respectively.

In 1952, Henkel developed the first Henkel process, in which potassium orthophthalate that could be manufactured by air oxidation of o-xylene was isomerized with a cadmium catalyst in carbon dioxide under conditions of 1–8 atm and approximately 400°C to give potassium terephthalate. In 1958, this process was industrialized for the first time in the world by Kawasaki Kasei Chemicals in Japan. Henkel developed the second Henkel process for producing potassium terephthalate and benzene by disproportionation of potassium benzoate. In 1963, this process was industrialized for the first time in the world by Mitsubishi Kasei in Japan. In this case, benzoic acid was produced by air oxidation of toluene (direct oxidation of the side chain methyl group in the presence of a cobalt salt catalyst), a process that was not available in the period of coal tar chemistry (toluene side-chain chlorination process).

In 1950, Imhausen in Germany developed a very sophisticated process for manufacturing DMT. According to this process, one of the methyl groups of p-xylene is air oxidized into p-toluic acid in the presence of a cobalt naphtenate catalyst; after it is methylesterified, another methyl group is air oxidized and the resulting substance is methylesterified again. This DMT process was industrialized by Hercules in the United States and many other companies around the world. It has the advantage that the purity of DMT, unlike that of terephthalic acid, can be increased by distillation. In polymerization, it is also advantageous that the reaction proceeds by transesterification between DMT and EG. However, because methanol is produced as a byproduct, it must be returned to DMT plants for reuse.

In 1955, Scientific Design developed a process for manufacturing terephthalic acid by oxidizing p-xylene in an acetic acid solvent in the presence of a cobalt acetate or manganese acetate catalyst and a bromine compound promotor. This process was tested for industrialization at Amoco Chemical and was then industrialized by Mitsui Petrochemical Industries and Maruzen Petrochemical in 1958 and 1960, respectively. It was subsequently widely used all around the world.

Following the Amoco process, a process for manufacturing chloromethylbenzene from toluene, formaldehyde and hydrogen chloride and a process for manufacturing diisopropylbenzene from benzene and propylene were developed in 1960.

As mentioned above, the method of manufacturing terephthalic acid went through various changes, but the Amoco process finally gained global precedence as the means of direct oxidation of p-xylene. According to this process, terephthalic acid is polymerized with EG to give polyester. Because water is the only byproduct, unlike the DMT process, it does not require the collection of methanol. The Amoco process developed to a process for manufacturing highly purified terephthalic acid in the 1970s and the production scale of this process increased further from the 1990s onwards.

Oxidation of the second methyl group of m-xylene was as difficult as it was for p-xylene. However, m-xylene was air oxidized by the same process as was used for p-xylene to give isophthalic acid. Isophthalic acid industrialized by Oronite Chemical in 1955 was used as an auxiliary raw material for alkyd resin and unsaturated polyester.

2) Oxidation of hydrogen at the α-position of side chain alkyl groups

Hydrogen at the α-position of the side chain alkyl group of ethylbenzene or cumene is oxidized to give a peroxide. This process is important for manufacturing intermediates of styrene and phenol.

Phenol is an important raw material, not only for fine chemicals, such as dyes, pharmaceuticals, pesticides and explosives, but also for phenol resin. As an industrial organic chemical, it has been produced on a large scale since the period of coal tar chemistry. In petrochemistry, it was initially used as a raw material for nylon. It then became increasingly important as a raw material for synthetic detergents, bisphenol A (epoxy resin, polycarbonate resin), etc.

In 1890, phenol was industrialized by sulfonation process of benzene. As mentioned in Section 4.6.1, the chlorobenzene and Raschig processes were subsequently industrialized in 1925 and 1935, respectively.

The process for manufacturing cumene is described in Section 6.1.2 (1) 4). When cumene is air oxidized at 130°C in the presence of an aqueous alkali solution, hydrogen at the α-position is oxidized to give cumene hydroperoxide. After unreacted cumene is removed by distillation, cumene hydroperoxide is concentrated and the concentrate is then treated with 10% sulfuric acid at 50°C to give phenol and acetone. Production of phenol by the cumene process has the advantage that the reaction conditions are much milder than for the existing processes and moreover, there are no wasted auxiliary raw materials. Meanwhile, synthesis of phenol by direct oxidation of benzene still remains one of the dreams of chemical researchers. Although many attempts have been made to realize this dream, none of them have have had the driving success of the cumene process in industrialization.

When ethylbenzene is air oxidized, hydrogen at the α-position is oxidized to give ethylbenzene hydroperoxide. This substance is reacted with propylene to give propylene oxide and α-phenylethyl alcohol. Styrene is obtained by dehydration of the latter compound. This method co-produces propylene oxide and styrene.

(4) Cycloparaffin chemistry

Throughout the technology system of industrial organic chemicals as shown in Fig 6.16, cycloparaffin chemistry has flourished little.

Adipic acid and ε-caprolactam are the only industrial organic chemicals that are produced on a large scale from cyclohexane. Both of them are C6 compounds. The reactivity of cycloparaffin is lower than that of olefins, but is higher than that of paraffin. Cyclohexane produced by the hydrogen reduction of benzene is the only cycloparaffin that is easily obtained in large quantities. It is very costly to synthesize other cycloparaffins or to separate them from petroleum.

Adipic acid and caprolactam were industrialized by DuPont and IG Farben in 1938 and 1940, respectively, during the coal tar chemistry era. Phenol was used as a raw material in both cases. Phenol is reduced with hydrogen to give cyclohexanol, which is oxidized with nitric acid to give adipic acid. Caprolactam was produced by Beckmann rearrangement from cyclohexanol via cyclohexanone and cyclohexanone oxime. The process from hexanol onwards was a combination of stoichiometric reactions for adipic acid and caprolactam, which subsequently remained unchanged for a long period of time.

At the beginning of the 1960s, it became possible to make large quantities of cyclohexane from benzene, and cycloparaffin chemistry started bearing fruit. As shown in Fig. 6.16, air oxidation and photonitrosation of cyclohexanone were industrialized on a large scale in the area of cycloparaffin chemistry.

As a result, the raw material changed from phenol to cyclohexane. Since a mixture of cyclohexanol and cyclohexanone is obtained by air oxidation of cyclohexane, adipic acid and caprolactam are both produced from the mixture.

The process for manufacturing caprolactam can be roughly divided into two halves. In the first half, cyclohexanone oxime is produced. In the second half, cyclohexanone oxime is allowed to undergo Beckmann rearrangement to give caprolactam. This process yields approximately 4.5 times more ammonium sulfate than caprolactam, because ammonium sulfate is obtained as a byproduct in the stages of manufacturing hydroxylamine, manufacturing oxime and Beckmann rearrangement. This is a serious disadvantage with this process. Accordingly, various methods have been developed to control the amount of ammonium sulfate byproduct. However, there are few processes that are still used to counter the oxime process. One of them is photonitrosation developed by Toray. It is a unique process in which cyclohexane, nitrosyl chloride and hydrogen chloride are reacted under photoirradiation to give cyclohexanone oxime hydrochloride. This is one of the rare examples in which a photochemical reaction is used for large-scale production of industrial organic chemicals. Since hydroxylamine is not used in this process, the amountof ammonium sulfate byproduct can be decreased. However, it is still obtained as a byproduct of the Beckmann rearrangement process.

In 1994, Enichem developed a process in which cyclohexanone oxime is directly produced from ammonia and cyclohexanone using hydrogen peroxide without using hydroxylamine in the presence of an MFI-type zeolite titanosilicate (TS-1 zeolite) catalyst (ammoximation process). Water is the only byproduct of this process. Meanwhile, Sumitomo Chemical developed high-silica MFI zeolite, a heterogeneous catalyst causing Beckmann rearrangement in the gas phase; the company industrialized a manufacturing process in which ammoxidation was combined with gas phase Beckmann rearrangement in 2003. Sumitomo Chemical became the first in the world in the 60-year history of caprolactam production to successfully produce caprolactam without any ammonium sulfate byproduct.

Meanwhile, Asahi Kasei developed an outstanding process for manufacturing cyclohexene by partial hydrogenation of benzene. Cyclohexanol is easily produced by the addition reaction of water to the double bond of cyclohexene. The addition reaction of water is a classic petrochemical process for alcohol production, mentioned in Section 6.1.2 (1). Asahi Kasei industrialized it in 1990.

(5) C1 chemistry

Chemistry stemming from C1 methane and syngas is called C1 chemistry. Following the oil crises, much attention was focused on potential oil depletion in the future. C1 chemistry has been actively studied since then. Figure 6.21 shows the current technology system. Many of these technologies have been available since before the creation of C1 chemistry.

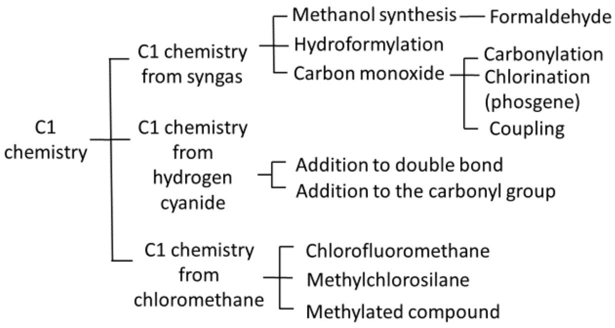


Fig. 6.21 System of C1 chemistry.

1) C1 chemistry from syngas

C1 chemistry from syngas includes many processes that have been available since before the creation of petrochemistry. In 1925, BASF industrialized production of methanol from carbon monoxide and hydrogen by high-pressure reaction (approximately 300 atm) in the presence of a zinc oxide-chromium oxide catalyst. Subsequently, it was also industrialized in the United Kingdom and the United States in the 1920s. In Japan, it was industrialized in 1932 based on studies by the Temporary Nitrogen Research Institute (formerly the Tokyo Industrial Research Institute, now the National Institute of Advanced Science and Technology) at the Hikoshima Factory of Gosei Kogyo (now Mitsui Chemicals). After the Second World War, methanol was produced by fundamentally the same process, but on a much larger scale owing to the introduction of centrifugal compressors. However, in the 1960s, ICI developed a low-pressure process (50–100 atm) using a copper-zinc-aluminum oxide catalyst and industrialized it on a large scale of 310,000 tons in 1972. Furthermore, Lurgi developed a process for manufacturing methanol by using a multitubular reactor in the presence of a copper oxide-zinc oxide catalyst. At present, large methanol plants are being built that are capable of producing 2 million tons annually.

The industrial production of formaldehyde from methanol by air oxidation in the presence of a copper or silver catalyst was already being performed at the end of the 19th century. Hydroformylation is described above in Section 6.1.2 (1) 5). The industrial manufacture of phosgene from carbon oxide and chlorine in the presence of an activated charcoal catalyst was already established in the 19th century. The manufacture of isocyanate from phosgene and amine was also already performed in the coal chemistry era, having started when the manufacture of polyurethane foam from TDI began in 1941. Since C1 phosgene is a bi-functional compound, it is reacted with different bi-functional compounds to give polymers. The industrialization of polycarbonate by condensation polymerization of phosgene and BPA was performed by Bayer and GE in 1957.

However, phosgene is toxic. Furthermore, neither isocyanate nor polycarbonate contains chlorine in the final product, as it is eliminated during production. As a result, expensive chlorine obtained by electrolysis is wasted. Accordingly, one of the most pressing goals for green chemistry from the 1990s onwards was the technological development of non-phosgene processes. The subsequent course of events is described in Section 5.6.3(2).

In acetylene chemistry, carbonylation using carbon monoxide as one of the Reppe reactions under high pressure was important for the synthesis of acrylic acid, acrylic acid ester, acrylamide, acrylic acid amide, etc. In olefin chemistry (see Section 4.5.2 (5)), BASF industrialized the synthesis of propionic acid from ethylene, carbon monoxide and water in 1952. However, it was not a large-scale product. BASF has continued studies on the method of manufacturing acetic acid by carbonylation of methanol since the company industrialized methanol in the 1920s. BASF developed molybdenum-nickel alloy (Hastelloy) resistant to corrosion and an industrial process using cobalt iodine as a catalyst in the 1960s. Meanwhile, Monsanto developed a metal carbonyl catalyst composed of rhodium and iodine in the 1960s and built the first 150,000 ton class plant in 1970. After that, the Monsanto process became the main process for manufacturing acetic acid by carbonylation of methanol. This process is the greatest successful example of C1 chemistry developed after the Second World War.

2) C1 chemistry from hydrogen cyanide

One large-scale petrochemical process using hydrogen cyanide is the synthesis of acetone cyanhydrin by adding hydrogen cyanide to the carbonyl group of acetone. It is the first process for manufacturing MMA;it has long been used and is widely used even now. However, because the production of MMA by the acetone cyanhydrin process is classified as (6) “Other organic synthetic chemistry,” it is not detailed here. Also, the addition of hydrogen cyanide to butadiene is an important process for synthesizing adiponitrile. It has already been described in Section 6.1.2 (1) 6).

3) C1 Chemistry from chloromethanes

Methyl chloride is used as a methylating agent for the synthesis of methyl cellulose, etc. It is also used for the synthesis of methylchlorosilanes by reaction with silicon in the presence of a copper catalyst. This process was developed by Rochow in 1941. Methylchlorosilanes are important raw materials for silicone. However, these polymers are not synthesized by C1 chemistry, because the methyl group of silicone is a side chain and its skeleton is composed of silicon and oxygen.

Fluorocarbons are synthesized from chloromethanes and hydrogen fluoride. However, the production of fluorocarbons has decreased as the number of substances regulated by the Ozone Protection Law has increased.

(6) Other organic synthetic chemistry (reactions of derivatives)

In addition to the above products directly produced from basic petrochemicals in olefin chemistry, aromatic hydrocarbon chemistry, cycloparaffin chemistry and C1 chemistry, petrochemistry also involves the production of many industrial organic chemicals by organic synthesis from primary derivatives made from basic petrochemicals. For example, there are many industrial organic chemicals made from ethylene oxide, ethylene dichloride/vinyl chloride, acetone, butyraldehyde, acrylonitrile, acrolein, phenol, nitrobenzene, cyclohexanone, etc. Technologies used for the synthesis of these chemicals should not simply be classified as petrochemical technologies, but as more comprehensive organic synthetic technologies. Detailed descriptions of these technologieshave been omitted here, because they are much older than petrochemical technologies, dating back to the creation of organic chemistry in the 18th century.

6.1.3 Technological system of polymers

As shown in Fig. 6.22, the system of polymer manufacturing processes can be roughly classified into chain polymerization and sequential polymerization. In chain polymerization, it is actually impossible to remove a substance that is changing to a polymer in the process of polymerization. Once chain polymerization starts in a low-molecular-weight raw material, only the unreacted monomer and the resulting polymer can be obtained, even if the polymerization process is discontinued partway through.

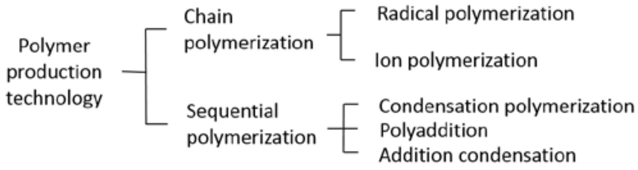


Fig. 6.22 System of polymer production technology.

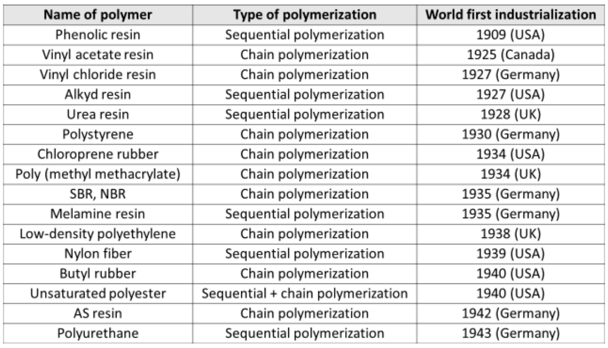
Chain polymerization is classified into radical polymerization and ionic polymerization. In radical polymerization, polymerization is performed using a radical-generating polymerization initiator. The radical initiator is partially bound to the end of the resulting polymer. In ionic polymerization, polymerization is started by ions. It is further classified into cationic polymerization, anionic polymerization, coordination anionic (metal complex) polymerization and metal oxide polymerization. Chain polymerization is applicable to compounds containing double bonds, such as olefins and vinyl compounds, heterocyclic compounds, such as ethylene oxide [Footnote 5], and aldehydes, such as formaldehyde.

By contrast, in sequential polymerization, a low-molecular-weight raw material reacts as a whole to give a substance of a slightly higher molecular weight, which then further reacts to finally give a polymer. If sequential polymerization is discontinued partway through, a substance of molecular weight in the intermediate stage of polymerization is obtained as an intermediate. Like reactions between low-molecular-weight substances with functional groups (such as esterification and amidation), sequential polymerization starts between monomers with at least two functional groups in a molecule and then intermediates continue reacting with each other. However, as the reaction proceeds, it becomes necessary for molecules with higher molecular weight to react with each other. As a result, viscosity is increased, thereby disturbing thesmooth progression of the reaction. Various modifications are needed for the industrial production of polymers.

As shown in Table 6.1, the industrialization of synthetic polymers started with phenol resin in 1909. Synthetic polymers were industrialized later than industrial organic chemicals. Although new synthetic polymers were industrialized from the 1910s to the 1920s, the concept of polymer had not yet been established. In 1920, based on the results of studies on natural rubber, etc., H. Staudinger insisted that a great number of small molecules are combined to form a large molecule; he advanced the concept of a giant molecule (macromolecule) in 1922. This theory was not accepted by the academic societies the day, giving rise to hot discussions. However, the idea rapidly penetrated into the academic societies in the early 1930s as a result of studies based on X-ray diffraction in the late 1920s, the proposal of a viscosity formula for polymer solutions by Staudinger-Ryusaburo Nozu in 1930, etc.

In 1928, supporting the macromolecule theory, W.H. Carothers started fundamental studies on the synthesis and physical properties of condensation polymers at DuPont. In 1934, P.J. Flory and Carothers independently advanced a theory of polycondensation. In 1937, Flory and G.V. Schulz independently advanced “a theoretical system of radical polymerization.” In the 1930s, the concept of polymers was established and the theoretical system of polymerization was completed. The background of polymerization processes was completed.

Table 6.1 Typical synthetic polymers industrialized before and during the Second World War



Name of polymer	Type of polymerization	World first industrialization
Phenolic resin	Sequential polymerization	1909 (USA)
Vinyl acetate resin	Chain polymerization	1925 (Canada)
Vinyl chloride resin	Chain polymerization	1927 (Germany)
Alkyd resin	Sequential polymerization	1927 (USA)
Urea resin	Sequential polymerization	1928 (UK)
Polystyrene	Chain polymerization	1930 (Germany)
Chloroprene rubber	Chain polymerization	1934 (USA)
Poly (methyl methacrylate)	Chain polymerization	1934 (UK)
SBR, NBR	Chain polymerization	1935 (Germany)
Melamine resin	Sequential polymerization	1935 (Germany)
Low-density polyethylene	Chain polymerization	1938 (UK)
Nylon fiber	Sequential polymerization	1939 (USA)
Butyl rubber	Chain polymerization	1940 (USA)
Unsaturated polyester	Sequential + chain polymerization	1940 (USA)
AS resin	Chain polymerization	1942 (Germany)
Polyurethane	Sequential polymerization	1943 (Germany)

Carothers not only advanced a theory, but also carried out synthesis and industrialization of polymers. In 1931, Carothers developed chloroprene rubber. This became the first monumental product to be industrialized based on the theory of macromolecules. Furthermore, DuPont announced the invention of 6,6-nylon in 1938 and industrialized it in the following year.

An interesting anecdote exists about the development of 6,6-nylon. In 1934, Carothers synthesized 5,10-nylon and suggested to his company superior that it would be a practical synthetic fiber. 5,10-Nylon is a polyamide in

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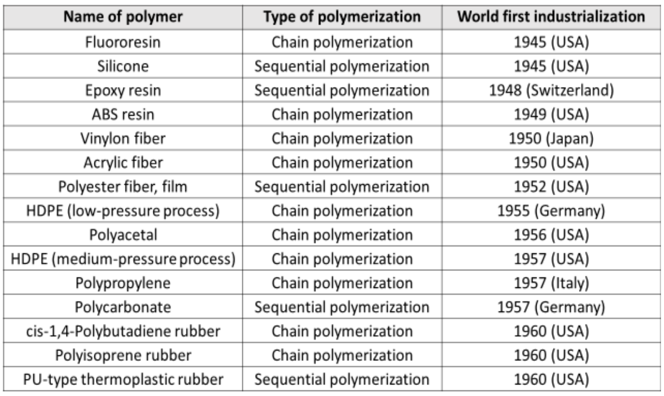
[Footnote 5] Cyclic compounds containing atoms other than carbon in the ring.

which C5 aliphatic diamine and C10 aliphatic dicarboxylic acid are polymerized. The raw material for C10 aliphatic dicarboxylic acid was castor oil. The company superior rejected his suggestion, because he considered that there could be a shortage of raw materials if nylon fiber were to meet with success in the future. Therefore, Carothers synthesized many other polyamides in which diamine was combined with carboxylic acid and from among these polyamides, he selected 6,6-nylon made from coal (phenol in those days). Obviously, he selected it based on the idea that molecular design not only includes methods of polymerization and performance of polymers, but also their profitability. Nylon was an epoch-making polymer, because the idea of molecular design was applied ahead of not only wholly aromatic polyamides, but also super engineering plastics and thermoplastic elastomers that were developed later.

After the Second World War, the consumption of polymers as materials for fibers, packages and daily necessities for consumer use showed a dramatic increase, starting in the United States (see Section 5.3.1 (4)). In particular, LDPE and polystyrene were supplied in large quantities by petrochemistry. In the 1950s, the trend toward domestic production of petrochemicals and the polymer revolution spread to Europe and Japan. At that time, polymer science also spread to the industrial world, and full scale technological development based on scientific theories commenced. As shown in Table 6.2, large-scale polymers such as ABS resin, acrylic fiber, polyester fiber, PET resin, HDPE, PP, polycarbonate, polyacetal, BR and EPDM emerged one after another over a period of 15 years between the late 1940s and the 1960s, resulting in an acceleration of the development of the petrochemical industry.

Table 6.2 Typical synthetic polymers industrialized before and during the Second World War



Name of polymer	Type of polymerization	World first industrialization
Fluororesin	Chain polymerization	1945 (USA)
Silicone	Sequential polymerization	1945 (USA)
Epoxy resin	Sequential polymerization	1948 (Switzerland)
ABS resin	Chain polymerization	1949 (USA)
Vinylon fiber	Chain polymerization	1950 (Japan)
Acrylic fiber	Chain polymerization	1950 (USA)
Polyester fiber, film	Sequential polymerization	1952 (USA)
HDPE (low-pressure process)	Chain polymerization	1955 (Germany)
Polyacetal	Chain polymerization	1956 (USA)
HDPE (medium-pressure process)	Chain polymerization	1957 (USA)
Polypropylene	Chain polymerization	1957 (Italy)
Polycarbonate	Sequential polymerization	1957 (Germany)
cis-1,4-Polybutadiene rubber	Chain polymerization	1960 (USA)
Polyisoprene rubber	Chain polymerization	1960 (USA)
PU-type thermoplastic rubber	Sequential polymerization	1960 (USA)

A great variety of polymer-manufacturing technologies, including those industrialized before the creation of petrochemistry, form a substantial pillar of petrochemical technology.

(1) Chain polymerization

Engineering technologies for chain polymerization are described first, following by explanations of radical polymerization and ionic polymerization reaction forms.

1) Manipulation technologies for chain polymerization

Polymerization is generally a large-scale exothermic reaction. Removal of the reaction heat is important especially in chain polymerization, because once polymerization has been initiated, the reaction will rapidly progress while generating heat. As shown in Fig. 6.23, manipulation technologies for chain polymerization are classified as bulk polymerization, solution polymerization, slurry polymerization, suspension polymerization and emulsion polymerization.

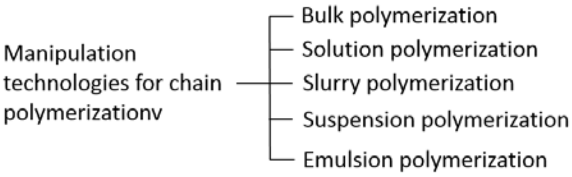


Fig. 6.23 System of manipulation technologies for chain polymerization.

Bulk polymerization is performed using a monomer alone in the absence of a solvent. This process is used for both radical polymerization and ionic polymerization. As a matter of course, removal of heat is important. Various processes have been developed, such as the bulk process, in which a monomer is used in large quantities as a solvent, and the fluidized bed process, in which a catalyst, etc. is added to an air stream of a monomer so that polymer particles are formed in the gas phase. HDPE, L-LDPE and PP have been actively manufactured by the gas phase process since the 1980s, chiefly because high performance catalysts for coordination anionic polymerization were developed.

In solution polymerization, the heat can be removed with a solvent and viscosity can be made lower than in bulk polymerization. However, the solvent must be separated from the polymer after polymerization. In the case of solution products such as adhesives, the solution after polymerization is used as it is. This process can be used for both radical polymerization and ionic polymerization.

Slurry polymerization is often used for ionic polymerization. Since a catalyst is suspended in a solvent and the resulting polymer is also suspended in it, the reaction solution as a whole becomes slurry. Due to the fact that the heat is removed by the solvent, the viscosity can be made lower than in solution polymerization.

Suspension polymerization is often used for radical polymerization. Water is usually used as a solvent. A monomer is suspended in a solvent and polymerization is started by dissolving a polymerization initiator in the suspended monomer. Heat can easily be removed, because polymerization proceeds while the monomer is suspended. This process is often used for the industrial production of vinyl polychloride.

Emulsion polymerization is also often used for radical polymerization. Since water is used as a solvent and since a monomer is emulsified with a surfactant, droplets are at least 1 unit smaller in size and heat can be removed more easily than in suspension polymerization. An initiator and a catalyst for polymerization are dissolved in a solvent and made to enter the emulsified micelles to initiate polymerization. After polymerization, an emulsion is formed. Emulsion polymerization is often used for the production of synthetic rubber, resin for coatings (emulsion coatings) and adhesives.

None of these polymerization manipulation technologies can be deemed as the best, because it varies with each polymer. For example, LDPE has always been manufactured by bulk polymerization since this process was developed. The method of manufacturing polyvinyl chloride changed from emulsion polymerization to suspension polymerization. HDPE and PP were initially produced by solution polymerization and slurry polymerization, but as catalysts improved, these processes were subsequently replaced by bulk polymerization using a monomer as a solvent and then by bulk polymerization using a gas phase fluidized bed. However, slurry polymerization, etc. are used even now for convenience in making some grades. SBR is produced by emulsion polymerization in radical polymerization, but by solution polymerization in anionic polymerization. Simply, manipulation technologies vary with each type of polymerization. As a result, the performance of the product also varies accordingly.

2) Radical polymerization

Radical polymerization has a long history. At first, it was used for the production of vinyl acetate resin, polyvinyl chloride and other such products that were developed in the 1920s. It can be very widely applicable to both polar and nonpolar monomers. High-pressure polymerization of ethylene (formation of LDPE), discovered in the 1930s, is also radial polymerization. The widely distributed molecular weight and large branched structure of LDPE represent well the characteristics of radical polymerization. As shown in Table 6.1 and 6.2, most of the typical polymers produced by radical polymerization, such as polyvinyl chloride, vinyl acetate resin, polystyrene, AS resin, ABS resin, LDPE, polymethyl methacrylate, chloroprene rubber, SBR, NBR, fluororesin and acrylic fiber, were already available before 1950. These polymers did much towards the full-scale development of petrochemistry from the 1950s onwards. However, prior to that, the development of the basic technology for radical polymerization had already been advanced by monomers made using coal chemistry.

Peroxides and azo compounds are often used as polymerization initiators. Since these compounds can generate radicals in response to heat, light (including ultraviolet rays and electron beams) and a combination of oxidation and reduction (redox initiator), they can initiate polymerization under various conditions. These initiators are used not only for the manufacture of polymers at plants, but also for the formation of photosensitive polymers for dental use, etc., for which polymerization at the site of use is preferred.

The termination of radical polymerization used to be uncontrollable, because it occurs due to radical transfer (chain transfer) or recombination. For this reason, polymers produced by radical polymerization were characterized by wide molecular weight distribution. However, living radical polymerization developed in the 1990s, unlike in existing technologies using polymerization initiators, made it possible to generate all polymer terminals at the same probability owing to radical generation from a stable covalent species (dormant species); moreover, radical concentrations can be kept low to control termination. Living radical polymerization began to be used in the 2000s, but it has only been applied to a relatively small amount of functional polymers. No new large-scale polymers have been developed using this method.

3) Ionic polymerization

As shown in Fig. 6.24, ionic polymerization is classified into cationic polymerization, anionic polymerization, metal oxide polymerization and coordination anionic polymerization. The molecular weight distribution range is narrower for ionic polymerization than for radical polymerization.

In cationic polymerization, the growth terminal of the polymer is a cation. Catalysts for cationic polymerization include Lewis acids, such as boron fluoride and aluminum chloride, protonic acids, such as sulfuric acid and phosphoric acid, Lewis acids combined with a halogenated alkyl or water as a cocatalyst, etc.. Monomers that undergo cationic polymerization are generally double-bond compounds with an electron-donating group. The polymerization of isobutylene is a typical industrial example of this type of polymerization.

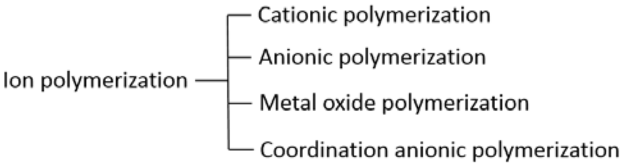


Fig. 6.24 System of ion polymerization.

In anionic polymerization, the growth terminal of the polymer is an anion. Catalysts for anionic polymerization include alkali metals, such as metal potassium and sodium, metal alkyls, such as butyl lithium, alkali amides, such as sodium amide, Grignard reagents, etc. Monomers that undergo anionic polymerization are generally double-bond compounds with an electron attractive group. Polymerization of styrene, butadiene, acrylonitrile, etc. can be performed by anionic polymerization. Since cyanoacrylic acid esters used for instant adhesives have a strong electron-attractive group, anionic polymerization is initiated by airborne moisture, resulting in solidification and adhesion. In this case, polymerization commences with water acting as a base.

Ring-opening polymerization of heterocyclic compounds, such as ethylene oxide, is also one type of ionic polymerization. Formation of polyacetal by polymerization of formaldehyde and by copolymerization of formaldehyde and ethylene oxide are also ionic polymerization processes.

Unlike in radical polymerization, no termination reaction due to recombination occurs in ionic polymerization, because the polymer growth terminals with the same electric charge repel each other. Also, because there are counter ions at the growth terminals, termination reaction due to chain transfer is unlikely to occur. Therefore, living polymerization can be performed. For example, on completion of ionic polymerization of styrene, a block copolymer can be made by polymerization of isoprene from the growth terminal of polystyrene. Styrene- and olefin-based thermoplastic elastomers are made using this technology.

Metal oxide polymerization is used for polymerization of ethylene under medium pressure. In 1950, Standard Oil (Indiana) discovered the formation of HDPE when trying to perform oligomerization of ethylene under moderate conditions in the presence of a silica-supported molybdenum oxide catalyst. At the same time, Phillips also obtained HDPE by using a silica- or alumina-supported chromium oxide catalyst. This process of polymerization can produce polyethylene under milder conditions than the existing high-pressure radical polymerization process for LDPE. It was industrialized in 1957 and has been used as a method of manufacturing HDPE ever since. However, metal oxide polymerization had no uses other than ethylene. When it is applied to propylene, approximately 10% solid PP is obtained, but the remainder is a liquid polymer that is useless.

4) Coordination anionic polymerization

Coordination anionic polymerization is one type of ionic polymerization. This process is described separately because it is particularly important in petrochemistry. In coordination anionic polymerization, the growth terminal of a polymer (anion) is coordinated with a catalyst to form a complex. In 1953, this polymerization process began with Ziegler’s successful polymerization of ethylene at ordinary temperature and atmospheric pressure in the presence of a triethyl aluminum-titanium tetrachloride catalyst. Like polyethylene obtained in the presence of a metal oxide catalyst, the resulting polymer was HDPE. In 1955, Natta succeeded in the formation of stereoregular polymers from α-olefins such as propylene and styrene in the presence of triethyl aluminum combined with titanium trichloride. Ziegler-Natta catalysts, shown in Table 6.2, were subsequently widely used to industrialize HDPE in 1955, PP in 1957, cis-1,4-polybutadiene (BR) and cis-1,4-polyisoprene (IR) in 1960 and EPDM in 1961.

Coordination anionic polymerization is a representative petrochemical technology because it has been used to produce numerous products and moreover, it has done much towards the technological development of petrochemistry since the 1960s (Fig. 6.25). In 1968, Mitsui Petrochemical Industries developed an alkyl aluminum-magnesium chloride-supported titanium chloride catalyst. The activity of this catalyst was more than 100 times higher than the first-generation Ziegler-Natta catalyst. As a result of this development, decalcification, which had been essential for reactions with Ziegler-Natta catalysts, became unnecessary. Furthermore, in 1975, Mitsui Petrochemical Industries and Montedison jointly succeeded in selectively making highly stereospecific active sites by letting an electron donor, such as ethyl benzoate, act on a catalyst. Since the Ziegler-Natta catalyst is a solid, its catalytic activity varies with each crystal surface (multisite). The active sites of this catalyst were selectively specified by using additives. As a result, it became unnecessary to remove nonstereoregular PP formed during polymerization in the presence of the Ziegler-Natta catalyst. This highly active and highly stereoregular catalyst is called the second-generation Ziegler-Natta catalyst. As a result of this development, the ranges of molecular weight distribution of HDPE and PP have been dramatically narrowed, resulting in marked improvements in quality (see Section 5.6.3 (1)).

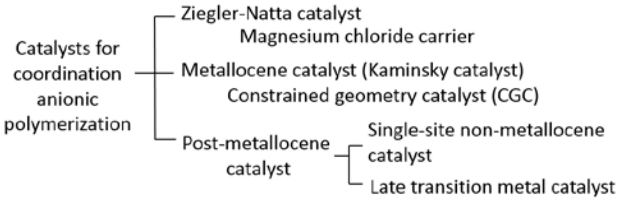


Fig. 6.25 Change of coordination anionic polymerization catalyst.

Manufacture of L-LDPE similar to LDPE by copolymerization of ethylene with α-olefin was industrialized by DuPont Canada in 1960. However, the quality of the product was lower than existing LDPE. In contrast, L-LDPE manufactured using the second-generation Ziegler-Natta catalyst was superior to LDPE in uniformity of composition distribution and also in performance. In 1979, UCC developed a method of manufacturing L-LDPE by the gas phase fluidized bed process. In the 1980s, L-LDPE achieved rapid growth, taking over a considerable part of the LDPE market. Also, because construction costs and operation costs were both lower than for high-pressure LDPE facilities, the L-LDPE process was exclusively adopted by new petrochemical industries in the Middle East and Asia. Due to the second-generation Ziegler-Natta catalyst, it became possible to further increase the amounts of comonomers; consequently, VLDPE and ULDPE with much lower density than LDPE were industrialized as new types of polyethylene.

Table 6.3 Typical synthetic polymers industrialized from the 1960s

Name of polymer	Type of polymerization	World first industrialization
EPDM	Chain polymerization	1961 (UK)
Polyimide	Sequential polymerization	1964 (USA)
PPO	Sequential polymerization	1964 (USA)
Ionomer resin	Chain polymerization	1964 (USA)
Polysulfone	Sequential polymerization	1966 (USA)
Meta aromatic polyamide fiber	Sequential polymerization	1967 (USA)
PBT resin	Sequential polymerization	1970 (USA)
Para aromatic polyamide fiber	Sequential polymerization	1971 (USA)
PES	Sequential polymerization	1972 (UK)
Gas phase L-LDPE	Chain polymerization	1979 (USA)
PEEK	Sequential polymerization	1980 (UK)
Polyetherimide	Sequential polymerization	1981 (USA)
Liquid crystal polymer	Sequential polymerization	1984 (USA)
Metallocene polyethylene	Chain polymerization	1991 (USA)

In 1980, Kaminsky found out that the polymerization activity of a catalyst in which a reactant of triethyl aluminum with water (Methylalumoxane [MAO]) was combined with metallocene (cyclopentadienyl complex of zirconium, titanium, etc.) was more than 1 unit higher than the second-generation Ziegler-Natta catalyst. This became known as a metallocene catalyst (Kaminsky catalyst) (see Section 5.7.4 (3)). The metallocene catalyst is a single-structure metal complex having a single active site (single site). Accordingly, the range of molecular weight distribution is narrower than the second-generation Ziegler-Natta catalyst. However, because improvements were also being made to the second-generation Ziegler-Natta catalyst, the metallocene catalyst was not used in the industrialization of polyethylene until 1991. Due to its superior merits, the metallocene catalyst is used in the production of elastomers, such as EPR and EPDM.

Organometallic complex catalysts foreshadowed by the Ziegler-Natta catalyst began to attract much more attention after the development of the metallocene catalyst. Many improvements and modifications are being made to these catalysts even now. A constrained geometry catalyst aimed at improving stereoregularity by controlling the structure around the active site has been developed and industrialized as a modification of the metallocene catalyst.

Figure 6.25 summarizes the status of catalysts for coordination anionic polymerization. It can be expected that these catalysts will develop further in the future. As an indication of future development, post-metallocene catalysts have already begun to develop. These are mentioned in Section 6.2.

(2) Sequential polymerization

As shown in Fig. 6.22, sequential polymerization is classified into condensation polymerization, polyaddition and addition condensation. The most typical reaction form of sequential polymerization is condensation polymerization (polycondensation). Condensation polymerization proceeds while polyfunctional monomers are performing condensation on each other by releasing a simple low-molecular-weight substance, such as water or hydrogen chloride. Formation of polyurethane by the reaction of polyol with a polyisocyanate compound is a modification of condensation polymerization. This reaction is also called polyaddition, because no simple low-molecular-weight substance is eliminated and a urethane bond is formed by the reaction between the hydroxyl and isocyanate groups. Meanwhile, if phenol resin, urea resin or melamine resin is formed, the reaction is called addition condensation. In this case, polymerization proceeds as follows: formaldehyde is added to active hydrogen at the ortho or para position of phenol or to active hydrogen of the amino group of urea or melamine to give a methylol group ($-CH_2OH$), which is then reacted with active hydrogen and then dehydrated (condensed) to give a methylene bond ($-CH_2-$). It also proceeds if the methylol groups dehydrate (condense) each other to give an ether bond

(-CH_2OCH_2-). If addition and condensation are repeated, a two-dimensional prepolymer will be formed depending on the conditions, followed by the formation of a three-dimensional crosslinked polymer by heating or pH change.

As shown in Table 6.1, addition condensation is the oldest method of polymerization, created before the period of petrochemistry. By this process, phenol resin - the first synthetic polymer, urea resin and melamine resin were industrialized in 1909, 1928 and 1935, respectively. Phenol resin was probably the first synthetic polymer to familiarize people with plastics, during the coal chemistry period before the creation of petrochemistry. Since phenol resin had the drawback of turning brown, it was colored black and used mainly for black telephones and bulb sockets. As urea resin showed no such discoloration, it was used in large quantities for white or colored tableware, buttons and electrical parts. In Japan, phenol resin and celluloid resin were typical plastics of the time before the Second World War. Urea resin became a typical plastic after the Second World War until the mid-1950s (see Section 5.3.3 (1)). Transparent and heat-resistant melamine resin was often used for decorating the surfaces of laminated plates made of phenol resin. However, it was time-consuming to mold phenol, urea and melamine resins to thermosetting resins by addition condensation; accordingly, the practice of using these resins as raw materials for molding daily necessaries and electrical parts was discontinued in the 1950s, when thermoplastic resins, such as polyethylene and polystyrene, began to be supplied in large quantities. However, even now these resin products still play an important role in manufacture of adhesives for plywood and laminates.

Nylon (polyamide), industrialized in 1939, was the first polymer made by condensation polymerization and polyaddition. As described above, nylon played a significant role in verifying and establishing the concept of polymers. Tables 6.1 and 6.2 show the polymers made by the industrialization of condensation polymerization and polyaddition, following on from nylon, unsaturated polyester, polyurethane, silicone and epoxy resin, which were developed before the full-scale development of petrochemistry. Since the 1950s when petrochemistry started coming into fruition, large-scale polymers have also been developed, such as polyester (PET), which is at present comparable in production to the four major general-purpose resins (PE, PP, PVC and PS), and polycarbonate, used as a more general application of an engineering plastic from the 1990s onwards. From the 1960s onwards, to meet the needs of the market for strong, heat-resistant polymers, as shown in Fig. 6.26, engineering plastics, such as polyphenylene oxide (PPO) and PBT, super engineering plastics, such as polyimide, PES, PEEK, polyether imide, and liquid crystal polymers and metha- and para-based aramid fibers were developed by condensation polymerization. In particular, super engineering plastics are polymers whose molecules are designed so that they have both high strength/high heat resistance and high forming processability required for thermoplastics. Condensation polymerization has the advantage of easy molecular design.

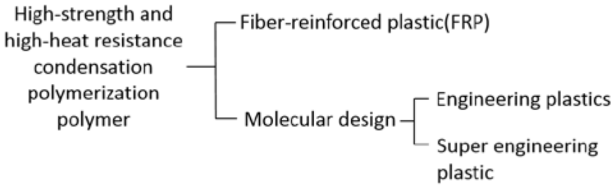


Fig. 6.26 Technology system of high-strength and high-heat resistance condensation polymerization polymers.

In terms of manipulation technology for condensation polymerization, the monomer and resulting polymer are usually heated above their melting points to perform polymerization in a molten state. This process corresponds to bulk polymerization in chain polymerization. Since condensation reaction is reversible, it is important to immediately remove the resulting condensed low-molecular-weight substance, such as water, from the reaction system. For this reason, polymerization is often carried out under reduced pressure. The molecular weight of PET may be insufficient for many uses if it is produced by normal condensation polymerization in a molten state under reduced pressure. Therefore, its molecular weight is further increased by solid-phase polymerization. In the case of polyester, condensation polymerization may be performed by transesterification between a diester monomer and polyol. Since low-molecular-weight monool is eliminated, it must be removed.

Meanwhile, aromatic polyamide fibers are made by low-temperature solution polycondensation in the presence of a polar solvent, such as DMF and N-methylpyrrolidone. This technology corresponds to solution polymerization in chain polymerization. In this case, it is important to increase the degree of polymerization as much as possible by dissolving the resulting polymer. After polymerization, spinning can also be carried out. Interfacial polymerization is also performed, in which condensation polymerization is carried out on the intersurface of two solvents that are insoluble in each other. For example, BPA is dissolved in sodium hydroxide solution, while phosgene is dissolved in methylene chloride. Since methylene chloride and water are insoluble in each other, two phases are formed. Condensation polymerization proceeds on the intersurface of the two phases to give polycarbonate.

6.2 New technological trends in petrochemistry

As mentioned in Section 5.5, it is said that petrochemistry technologically matured in the late 1970s. The superiority of steam cracking was established in the manufacture of olefins. Subsequently, because improvements were only made to increase the scale of production, investigations in pursuit of technological varieties decreased significantly in number. Since coal and fermentation chemicals were completely replaced by industrial organic chemicals, it became difficult to develop new technologies leading to any dramatic increase in the scale of productivity. However, from the 1970s onwards, technologies for manufacturing industrial organic chemicals showed steady development, although not so strikingly as was observed in the 1950s and 1960s. One such technology was olefin chemistry from C4 and C5 compounds that were not previously in demand. Another example was energy-saving low-pollution manufacturing technologies (see Section 5.6.3). Technological innovations continued in polymer technology as follows: the second-generation Ziegler-Natta catalyst was industrialized in the 1970s, L-LDPE as a large-scale new product in the 1980s and the metallocene catalyst in the 1990s; many super engineering plastics, high performance fibers and functional resins were developed. Meanwhile, due to the steady accumulation of technological modifications, such as living polymerization and block polymerization, PP achieved marked growth in the 1980s and as a result, the demand for olefins was corrected from monopolar concentration on ethylene that had continued up until the 1960s. The demand for isobutylene (a raw material for MMA and MTBE) and the demand for 1-butylene (an auxiliary raw material for L-LDPE) also increased. The use of olefins overall was accelerated, and the petrochemical industry became very comprehensive, as discussed in Chapter 3.

Meanwhile, the two oil crises in the 1970s meant that subsequent attention was focused on the need to develop technology to counter the depletion of petroleum resources. While coal is reserved in large quantities under ground, its handling is difficult. Therefore, studies have been conducted to develop chemical reactions directly producing industrial organic chemicals from methane or other alkanes as natural gas, which have the second greatest reserve after coal and are easy to handle. Under these circumstances, many technological innovations have occurred in the petrochemical industry since the 1990s, although their historical value has not yet been established. This technology has the potential to create new types of petrochemistry with product categories and forms of production that differ from existing petrochemistry that has been prevalent around the world since the 1950s, that is, technology in which basic petrochemicals are produced by steam cracking and then transported by pipeline to petrochemical complexes manufacturing industrial organic chemicals and polymers.

6.2.1 Metathesis reaction of olefins

The metathesis reaction of olefins was found and developed as a triolefin process during the *Sturm und Drang* period of petrochemistry in the 1960s, but its value was unknown. Subsequently, the mechanism of the reaction was elucidated. It was found to be a reaction of double bonds, although the form of the reaction was unknown (see Section 6.1.2 (1)). Recombination of bonds occurs between two kinds of olefins. It is induced by a transition metal alkylidene complex catalyst (carbene complex). In 1967, Calderon et al. confirmed that a double-bond was cleaved to give a new double bond in the presence of a catalyst composed of WCl_6 and $EtAlCl_2$. This confirmation made the metathesis reaction well known. In 1971, Chauvin suggested a mechanism for this reaction. Around that time, the reaction began to be utilized as a petrochemical process in the presence of a Ziegler-type catalyst composed of tungsten or molybdenum combined with alkyl aluminum, etc. In the 1990s, Schrock and Grubbs et al. developed a highly active alkylidene complex catalyst of molybdenum and ruthenium that could tolerate functional groups with high polarity. Since then, this catalyst has been widely used, not only for petrochemistry, but also for organic synthetic reactions.

As shown in Fig. 6.27, there are three successful examples of the application of metathesis reactions in petrochemistry.

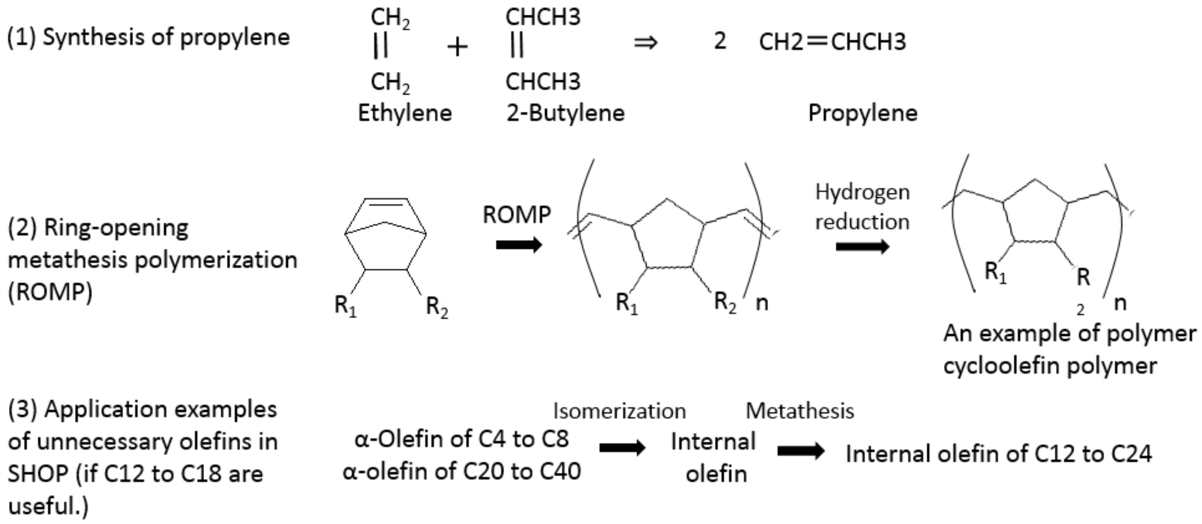


Fig. 6.27 Examples of metathesis reactions utilized in petrochemistry.

(1) Synthesis of propylene

The production of propylene by the metathesis reaction of ethylene with 2-butylene was industrialized for the first time in 1970. However, it was not until the mid-1980s that this reaction became used on a fully-fledged scale. In the 1990s, this process was used for the large-scale production of propylene. Due to the increased demand for propylene, propylene also began to be actively manufactured at petrochemical complexes in Japan by steam cracking of naphtha from 2-butylene, for which there was little demand. Several plants producing 150,000 tons of propylene a year by the metathesis process have been built in Japan. The production of propylene at these plants is significant, comparable to the amount of propylene obtainable from plants producing 300,000 tons of ethylene by steam cracking of naphtha. In the Middle East, where propylene cannot be obtained because ethane is used as a raw material, plants have been built at which ethylene is dimerized to give n-butylene, which is then subjected to metathesis reaction with ethylene to give propylene.

(2) Metathesis polymerization

The second typical example of metathesis reaction application in petrochemistry is metathesis polymerization. Cyclic olefin is subjected to ring-opening metathesis polymerization (ROMP) in the presence of a Ziegler-type catalyst to give a polymer, which is then hydrogenated to give an optical material outstanding in transparency, heat resistance and size stability. Many chemical companies have been actively seeking a new market for this area. If a Grubbs catalyst that is highly resistant to polar functional groups is used, various functional groups can be introduced and living polymerization can also be performed. Accordingly, attempts have been made to make use of this process for the synthesis of functional polymers.

(3) Efficient synthesis of α-olefins

Metathesis reaction was also applied to a method of efficiently synthesizing α-olefins (see Section 3.4.2 (7)). This is the synthetic higher olefin process (SHOP) developed by Shell. Ethylene is oligomerized to give α-olefins with various numbers of carbon atoms. There are limited higher alcohols with carbon numbers that are useful for surfactants, lubricants, etc. In contrast, the SHOP is a sophisticated process in which metathesis reaction and isomerization/hydroformylation in the presence of a cobalt catalyst take place repeatedly to avoid the formation of useless α-olefins. After an α-olefin with a useful carbon number atom is removed, the remaining olefins with longer and shorter carbon chains are isomerized (into internal olefins). Reorganization is then performed by metathesis reaction in such a way so that the olefin carbon atoms are added and then divided by two. From this, internal olefins with useful numbers of carbon atoms are separated again. The resulting internal olefin is hydroformylated in the presence of a cobalt catalyst to give terminal aldehyde. This is reduced to give alcohol, which is then dehydrated to give an α-olefin with a useful number of carbon atoms. If this procedure is repeated, only α-olefins with necessary carbon numbers are obtained.

It is also expected that metathesis reaction will be further applied to petrochemical processes, such as the synthesis of styrene by metathesis reaction of stilbene formed by dimerization of toluene by oxidative dehydrogenation with ethylene. Monoolefins and dienes with slightly complicated molecular structures have been produced by metathesis reaction and have already been industrialized as intermediates for fine chemicals.

6.2.2 Propylene-targeted production technology

As mentioned in Section 5.7.4 (1), the demand for propylene increased relative to that for ethylene in the 1980s. A shortage of propylene became apparent in the United States, where it was obtained as a byproduct of the fluidized catalytic cracking (FCC) process mainly for producing gasoline, and also in countries where propylene was obtained as a byproduct of ethylene production by steam cracking of naphtha. Accordingly, the 1990s saw the start of large-scale production of propylene by metathesis reaction, as mentioned in the preceding section. In the 1990s, production of propylene by catalytic dehydrogenation of propane also started. Although this process was at first not considered to be able to rival the byproduct processes, steady improvements have been made with respect to catalysts and processes.

In contrast to FCC, deep catalytic cracking (DCC), which aims at increasing the yield of propylene rather than decreasing the yield of gasoline, was developed and industrialized in China. Subsequently, this process has also been developed in many countries other than China. It is also known as reinforced fluidized catalytic cracking.

In China, the petrochemical industry experienced a sudden rise due to technology imports and capital injection from other countries from the 1990s onwards. To prevent an increase in the dependence on other countries for petroleum, China planned to build plants for industrial chemical products from coal, mainly in inland areas such as Inner Mongolia. One example was the MTP process for manufacturing propylene from methanol derived from coal. In 2010, a 500,000-ton class MTP plant was built using imported technology and used for manufacturing PP. However, because it was built as part of the economical security policies of China, there is little likelihood of this plant immediately realizing competitiveness. Since oil refining companies and plant engineering companies in developed countries originally made strenuous efforts to develop the MTP process, its industrialization in the inland areas of China should be regarded as experimental in a special market with only a few rival companies. However, because methanol can be produced much more cheaply and on a much larger scale from natural gas than from coal in natural gas-producing countries, the development of the MTP process to use cheap methanol as a raw material is, in itself, an interesting part of C1 chemistry, mentioned below.

6.2.3 C1 chemistry

Before the Second World War, syngas was exclusively made from coal. Since the end of the war, it has been made from petroleum and natural gas. Unlike petroleum, natural gas is produced at remote places far from consumption areas; accordingly, its development is often difficult due to difficulty in transportation. To solve this problem, there has been a growing trend to manufacture syngas and produce methanol and ammonia on a large scale at production sites for natural gas.

As already mentioned in Section 6.1.2 (5) 1), one of the consumers of cheap methanol produced as described above was a process for manufacturing acetic acid by carbonylation of methanol, industrialized in 1970. Due to the major success of this process, and due to the petroleum crises of the 1970s, research and development of C1 chemistry were actively conducted from the 1970s to the 1980s. However, for the time being, the only outcome has been to prove thedifficulty of C1 chemistry.

Meanwhile, attention has been focused on the synthesis of dimethyl oxalate by oxidative carbonylation of carbon monoxide, methanol and oxygen (Section 3.4.1 (3)), developed by Ube Industries in the 1970s as a method of synthesizing C2 compounds by coupling carbon monoxide. Dimethyl oxalate is hydrogen reduced to give EG and methanol. This process was industrialized in 1978. Recently, many plants producing EG by this process have been built in China. These Chinese plants use carbon monoxide from coal. Ube Industries also synthesized dimethyl carbonate by the same process. The importance of dimethyl carbonate has been increasing as an electrolyte for lithium ion secondary batteries and also as an alternative for phosgene (a starting material for manufacturing polycarbonate by the nonphosgene process).

6.2.4 Paraffin chemistry

Paraffins (alkanes) other than methane, such as ethane, propane and butane, have been converted to olefins by steam cracking, etc. before use due to their markedly low reactivity. However, because paraffin is cheaper than olefins, attempts have been made to develop a method of directly manufacturing industrial organic chemicals from paraffin.

The first successful example of paraffin chemistry was the synthesis of acetic acid by liquid-phase oxidation of propane, butane and pentane, developed by Celanese in 1952. According to this process, acetic acid is manufactured by dissolving a catalyst, such as cobalt acetate or chromium acetate, in an acetic acid solvent and then blowing raw material gas and air into the solution. In addition to acetic acid, byproducts obtained include acetaldehyde, acetone, MEK, ethyl acetate, formic acid and propionic acid. More byproducts are obtained in paraffin chemistry than in olefin chemistry, because the conditions for reaction are severer for paraffin chemistry.

In 1962, Distillers industrialized processes for synthesizing acetic acid from light naphtha in the presence of a manganese naphthenate catalyst. However, these processes for manufacturing acetic acid competed with oxidation of acetaldehyde from ethylene in the 1960s and were overwhelmed by carbonylation of methanol from the 1970s onwards.

The second successful example was the production of maleic anhydride by oxidation of n-butane. Maleic anhydride is a mid-scale industrial organic chemical that is used as a raw material for unsaturated polyester and also for synthesis of fumaric acid and malic acid. In the coal chemistry period, it was already produced in small quantities exclusively by air oxidation of benzene in the presence of a vanadium pentoxide catalyst. This reaction was similar to the process for manufacturing phthalic anhydride from naphthalene (see Section 4.6.2), and maleic anhydride was also obtained as a byproduct of phthalic anhydride. Oxidation of benzene was a wasteful process, because two carbon atoms of benzene were made into carbon dioxide. Therefore, a method of manufacturing maleic anhydride from n-butylene was developed in 1962. Vanadium pentoxide-phosphoric acid was used as a catalyst. However, after Monsanto developed a method of manufacturing maleic anhydride from n-butane in 1974, the benzene and n-butylene processes were both rapidly replaced by the butane process. Vanadium pentoxide-phosphoric acid was also used as a catalyst for this method.

The third successful example of paraffin chemistry was the co-production of t-butyl peroxide and t-butyl alcohol by oxygen oxidation of isobutene. t-Butyl peroxide is used for oxidation of propylene to give propylene oxide and t-butyl alcohol. t-Butyl alcohol was in great demand from the 1980s to the 1990s. This was due to MTBE being used as a gasoline additive. However, the demand for t-butyl alcohol decreased rapidly after adding MTBE to gasoline was prohibited in the early 2000s, meaning there was no longer any use for this technology.

As mentioned above, the only successful examples of paraffin chemistry had been for paraffins with four or more carbon atoms. However, in the 2000s, promising processes for paraffins with C2 or C3 were developed one after another. This was pioneered by the direct synthesis of acrylonitrile by ammoxidation of propane developed by Asahi Kasei. Industrial production was started by a subsidiary of Asahi Kasei in Korea in 2007 and after that in Thailand. A plan is also being pushed forward to industrialize it in Saudi Arabia. The catalyst for this process is a complex oxide of molybdenum, vanadium, niobium, etc. Following on from the ammoxidation of propane, processes have been rapidly developed for direct oxidation of propane for manufacture of acrylic acid and direct oxidation of ethane for manufacture of acetic acid. The oxychlorination process, in which vinyl chloride is directly obtained from ethane, chlorine and oxygen, is also undergoing development. Although these processes were expected to be industrialized in the 2000s, none of them have been industrialized as yet. The issue lies with the large amounts of chlorinated hydrocarbon byproducts.

BP/UCC developed a process for manufacturing aromatic hydrocarbons by cyclodehydrogenation of propane and butane. In 1999, this process, also known as the Cyclar process, was industrialized in Saudi Arabia on a benzene production scale of 350,000 tons and a p-xylene production scale of 300,000 tons. Thus commenced production of aromatic hydrocarbons from paraffins with six or less carbon atoms.

As mentioned above, it was not until approximately 50 years after the synthesis of acetic acid by liquid-phase oxidation that paraffin chemistry began to rival olefin chemistry in any way.

6.2.5 Post-metallocene catalysts

With the industrialization of the single-site metallocene catalyst in contrast to the multi-site Ziegler-Natta catalyst in the 1990s, coordination anionic polymerization began to attract much attention again in the 1990s. As a result, various single-site non-metallocene catalysts and late transition metal catalysts were successively developed as post-metallocene catalysts in the latter half of the 1990s (Fig. 6.25). The former catalysts use ligands other than cyclopentadienyl, which is used in metallocene catalysts. Unlike the metallocene catalyst using early transition metals such as zirconium and titanium, the latter catalysts use late transition metals such as iron, nickel and palladium.

Many post-metallocene catalysts that are more active than the Ziegler-Natta and metallocene catalysts have been developed. It is especially promising that these catalysts are not easily fractured by water or polar monomers. The applicable monomers and conditions used to be limited to a large extent for ionic polymerization than for radical polymerization. It is expected that new large-scale polymers will be created by copolymerization of olefins with polar monomers.

6.3 History of petrochemical technology and epoch-making technologies

Since petrochemistry has long been closely related to industrial organic chemicals and polymers since even before its creation, it is considerably difficult to identify purely petrochemical processes using natural gas and petroleum as raw materials (petrochemical processes in the narrow sense). However, since Section 6.5 discusses the systematization of petrochemical processes, in this section we shall only review the history of petrochemical technology according to the narrow sense, using natural gas and petroleum as raw materials, and introduce those epoch-making technologies for petrochemistry.

6.3.1 History of petrochemical technology

To review the history of petrochemical technology, petrochemicals can also be classified three ways; namely, basic petrochemicals, industrial organic chemicals and polymers.

(1) Technologies for basic petrochemicals

Production of basic petrochemicals started at in the early 1920s with the production of ethylene by steam cracking of ethane in the United States. The ethane was separated from natural gas. This separation process was an application of the cryogenic distillation process developed in the industrial gas industry in the 1900s. The thermal cracking process for hydrocarbons was based on the thermal cracking technology for heavy oil that had been developed in the oil refining industry in the 1910s. However, unlike thermal cracking technology for heavy oil, the steam cracking process progressed from petroleum refining to petrochemistry due to the technological innovation in lowering the partial pressure of hydrocarbon by the addition of steam. The application of steam cracking was extended to include propane in the 1930s and naphtha in the 1940s. It took quite some time to widen the range of applications; this was because the types of basic petrochemicals produced by steam cracking rapidly increased with each increase in the number of carbon atoms in the raw material hydrocarbon, which meant it then became necessary to develop technologies for separating/refining them. Both production technologies and separation and refining technologies are important for basic petrochemicals, as mentioned in Section 6.1.1 (8). Steam cracking has been the most important manufacturing technology for ethylene since the 1920s. Although manufacture of ethylene by catalytic cracking of hydrocarbon has long been studied, it has not been industrialized yet.

The steam cracking of naphtha in petrochemistry has become a major supply source of not only ethylene but also propylene, butylene, butadiene, benzene and p-xylene. It is also worth noting that this process led to the started of production of basic petrochemicals not only in the United States, but all around the world, as mentioned in Section 5.3.2 (2). Steam cracking of naphtha was widely used in the 1950s in Europe and Japan, from the 1970s onwards in Asia and Latin America and in the 2000s in China. Meanwhile, steam cracking of ethane was only widely used in the Middle East in the 1980s.

Thermal cracking and catalytic cracking of heavy oil are petroleum refining technologies, because the main purpose is production of gasoline. These cracking technologies are associated with the generation of large amounts of waste hydrocarbon gas containing propylene and butylene.

Since there has long been less demand for propylene than for ethylene, the main supply source for it has been waste gas from steam cracking of naphtha, mainly for producing ethylene; in the United States and other countries, it has been waste gas from catalytic cracking of heavy oil, mainly for producing gasoline. In other words, propylene has been supplied by byproducts. However, from the 1990s onwards, the supply of propylene became insufficient; consequently, propane dehydrogenation and metathesis reaction (ethylene and n-butylene) were industrialized. The only main purpose of these technologies was the production of propylene.

Butadiene is mainly supplied by solvent extraction and extractive distillation from the C4 fraction produced by steam cracking of naphtha. This process was developed in the 1940s; modifications to it were developed one after another in the 1950s and the 1960s and have been used until now. In the United States, butadiene has also been produced since the 1930s by dehydrogenation of butylene from waste gas obtained by catalytic cracking of heavy oil. This technology may also be classified as a petrochemical technology.

Meanwhile, catalytic reforming of naphtha is a petroleum refining technology, mainly for producing high-octane gasoline. Catalytic reforming was widespread in the United States in the 1950s, followed by Europe and Japan. The technology for extracting aromatic hydrocarbons from reformate is a petrochemical technology that was developed in the 1950s. The production of aromatic hydrocarbons was industrialized using the distillation of coal tar in the mid-19th century. In the 1950s and the 1960s, approximately 100 years later, the main aromatic hydrocarbon supplier shifted from coal tar to petrochemistry, due to the development of two petrochemical technologies. These were the distillation of cracked gasoline by steam cracking of naphtha and the extraction of aromatic hydrocarbons from reformate. Further, petrochemical processes for producing individual aromatic hydrocarbon products came to include dealkylation of toluene (benzene), developed in the 1950s, and disproportionation of toluene (benzene and xylene) and isomerization of m-xylene (xylene), developed in the 1960s. Petrochemical technologies for separating individual aromatic hydrocarbon products came to include separation of p-xylene by crystallization (1940s), separation of p-xylene by solid adsorption (1970s), separation of m-xylene by complex formation (1960s), etc., in addition to various distillation technologies, including extractive distillation and azeotropic distillation.

A technology for producing syngas was originally developed in the 1910s as a syngas reaction of coke. Since the main purpose of this technology was to obtain hydrogen in order to synthesize ammonia, a water gas reaction was also carried out. In this water gas reaction, carbon monoxide was reacted with steam to give hydrogen and carbon dioxide. Syngas was made in large quantities to produce methanol in the 1920s and artificial petroleum by the FT process in the 1930s. In petrochemistry, production of syngas from hydrocarbons such as natural gas, propanone/butane, naphtha and crude oil went into full swing in the 1950s.

As mentioned above, the basic petrochemical product technologies manufactured from petroleum or natural gas became fully industrialized in the 1920s for ethylene, the 1940s for butadiene and the 1950s for propylene and aromatic hydrocarbon/syngas (Fig. 6.28).

(2) Technologies **for industrial organic chemicals**

As shown in Fig. 6.29, there are a large number of major industrial organic chemicals; furthermore, many of them have been industrially produced since before the creation of petrochemistry. Therefore, it is difficult to gain a sense of the overall flow of petrochemical technologies in the narrow definition. For this reason, the history of industrial organic chemicals is reviewed here according to the system of technologies used in Section 6.1.2 Technological system of industrial organic chemicals.

Addition reactions to the double bond of olefins by the sulfuric acid process began with the production of IPA in the 1920s and the production of butanol and ethanol in the 1930s. Also in the 1920s, the production of ethylene oxide, EG and propylene oxide began by the chlorohydrin process. The production of EDC by addition of chlorine was also performed in the 1920s, although it soon came to nothing. These processes were all stoichiometric reactions using highly reactive chemicals. In the 1930s, addition reactions using catalysts were developed one after another. For example, ethylene oxide was made by epoxy-addition of oxygen to ethylene; ethylbenzene and cumene were made by addition of benzene to ethylene; polymer gasoline was made by addition of olefins to olefins; alkylate gasoline was made by addition of isobutane to olefins and butyraldehyde was made by the oxo process with propylene. From the 1940s to the 1950s, alcohol was produced by direct hydration reaction to the double bond of olefins, while ether was produced by direct addition reaction of alcohol to the double bond of olefins.

Development of the epoxy addition process to the double bond of propylene was substantially delayed. In the 1960s, the Halcon process was developed, using peroxide. However, this process was not convenient, as the stoichiometric reaction produced propylene oxide along with byproducts (styrene, t-butyl alcohol, etc.). In the 1990s, the hydrogen peroxide process was developed, with water as a byproduct, and the above problem was solved. However, direct addition reaction with oxygen has not yet been industrialized.

Product	Before 1900	1900s	1910s	1920s	1930s	1940s
Syngas	Coke oven gas			Syngas reaction of coke		
Hydrogen cyanide	Castner process (metal Na, coke and ammonia)				Formamide process	
Acetylene			Carbide process			Arc process of natural gas
Ethylene			Thermal cracking of heavy oil	→ Waste gas utilization Ethane steam cracking	Dehydration of fermentation ethanol	Coke oven gas separation
						Pipe-type steam cracking of naphtha
Propylene			Thermal decomposition of heavy oil	→ Waste gas utilization		Pipe-type steam cracking of naphtha
						Heavy oil fixed-bed catalytic cracking
Butadiene					Acetaldehyde condensation process	Pipe-type steam cracking of naphtha
						Butylene dehydrogenation process
						Butane dehydrogenation process
Butylene			Thermal decomposition of heavy oil	→ Waste gas utilization		Heavy oil fixed-bed catalytic cracking
						Pipe type steam cracking of naphtha
Higher olefin						
Benzene	Coal tar distillation					Pipe-type steam cracking of naphtha
Mixed xylene						Pipe-type steam cracking of naphtha
p-Xylene						Crystallization separation process

Fig. 6.28 Technological history of basic petrochemicals (before 1900 – 1940s).

Product	1950s	1960s	1970s	1980s	After 1990s
Syngas	Steam reforming of natural gas by partial combustion, steam reforming				
Hydrogen cyanide	The Andrussow process using natural gas as raw material	AN byproduct of Sohio process			
Acetylene	Byproduct by steam cracking of ethane and naphtha	High-temperature steam cracking process of naphtha and crude oil			
Ethylene	Trial for various naphtha cracking processes	High-temperature steam cracking process of naphtha and crude oil			
Propylene	Heavy oil fluidized-bed catalytic cracking				Metathesis process Strengthening fluidized-bed catalytic cracking Propane dehydrogenation process MTP process
Butadiene					
Butylene	Heavy oil fluidized-bed catalytic cracking		Isobutane dehydrogenation	Separation from FT artificial petroleum	Ethylene dimerization
Higher olefin		Propylene tetramerization	Pyrolysis of n-paraffin Ethylene oligomerization	Separation from FT artificial petroleum	
Benzene	Catalytic reforming oil extraction of naphtha Toluene dealkylation process	Toluene disproportionation process			Cyclode-hydrogenation of propane/butane
Mixed xylene	Catalytic reforming oil extraction of naphtha	Toluene disproportionation			
p-Xylene		m-Xylene isomerization Octafining process	Solid adsorption separation process		m-Xylene isomerization HTI process

Fig. 6.28 Technological history of basic petrochemicals (1950s – after 1990s).

Product	Before 1900	1900s	1910s	1920s	1930s	1940s
Ethylbenzene					Aluminum chloride catalytic process	
Styrene					EB dehydrogenation process by alumina-chromia catalyst	
					EB side chain chlorination, dehydrochlorination process	
					Acetophenone process	
Methanol	Wood carbonization process			Coke-based syngas process		
Ethanol			Fermentation process		Sulfuric acid and hydration process of ethylene	Direct hydration process of ethylene
IPA				Sulfuric acid and hydration process of propylene		
Butanol			n Product by acetone-butanol fermentation process	n Product by condensation and reduction process of acetaldehyde	sec and tert Product from sulfuric acid and hydration process of n-butylene and isobutylene	
					n and iso Product from Co catalyst oxo reaction and reduction process of propylene	
Higher alcohol				High-pressure hydrogen reduction of oils and fats	n-Paraffin oxidation process	
EO				Chlorohydrin process	Silver catalyst direct oxidation process	
EG				EDC process and chlorohydrin process	EO water addition process	
PO				Chlorohydrin process		
Glycerin	Hydrolysis process of oils and fats					Epichlorohydrin process
Acetone	Decomposition process of wood carbonization Acetate of lime		Acetone-butanol fermentation process	Dehydrogenation process of IPA	Acetylene/steam process	
Acrylonitrile					Ethylene cyanohydrin process	
Acrylic acid					Ethylene cyanohydrin process	

Fig. 6.29 Technological history of major industrial organic chemicals. (Ethylbenzene – Acrylic acid before 1900 – 1940s)

Product	Before 1900	1900s	1910s	1920s	1930s	1940s
MMA				Acetone cyanohydrin process Propylene, chloroacetic acid process		
Acetaldehyde			Mercury sulfate catalyst hydration process of acetylene	Ethanol oxidation process		
Acetic acid	Wood carbonization process		Oxygen oxidation of acetaldehyde			
Vinyl acetate			Liquid-phase acetic acid addition process to acetylene	Gas-phase acetic acid addition process to acetylene		
Vinyl chloride				Alkali dehydrochlorination process of EDC	HCl addition process to acetylene by Mercury chloride catalyst	
Phenol	Coal tar distillation Sulfuric acid process of benzene			Chlorobenzene process	Raschig process	
Adipic acid					Phenol - cyclohexanol - nitric acid oxidation process	
Caprolactam					Phenol - anon - oxime - Beckmann rearrangement process	
Terephthalic acid						
Phthalic anhydride	Fuming sulfuric acid oxidation of naphthalene		Catalytic oxidation process of naphthalene			
Maleic anhydride			Phthalic anhydride byproduct recovery process		Catalytic oxidation process of benzene	

Fig. 6.29 Technological history of major industrial organic chemicals. (MMA – Maleic anhydride before 1900 – 1940s)

Product	1950s	1960s	1970s	1980s	After 1990s
Ethylbenzene	Phosphoric acid catalytic process	BF3-HF catalytic process	ZSM-5 catalyst process		
Styrene	EB dehydrogenation process of steam dilution by iron oxide catalyst		Halcon process (PO co-production process)		
Methanol	Natural gas-based syngas process				
Ethanol					
IPA	Direct hydration process of propylene				
Butanol		tert Product from Halcon process (PO co-production process)	tert Product from direct hydration process by acidic IM catalyst of isobutylene		
	n and iso Product from Reppe process (CO, water) of propylene		n Product from Rh catalyst oxo reaction (CO, hydrogen) and reduction process of propylene		
Higher alcohol	Ziegler-Alfol process		Oxo reaction and reduction process of higher olefin		
EO					
EG			Dimethyl oxalate reduction process		
PO		Halcon process (oxidation by peroxide)			Direct oxidation by hydrogen peroxide
Glycerin				Allyl alcohol process	Biodiesel byproduct
Acetone	Cumene process	Wacker atmospheric oxidation process of propylene			
Acrylonitrile	HCN addition process to acetylene	Sohio process (ammoxidation of propylene)			Ammoxidation process of propane
Acrylic acid	Modified Reppe process (carbonylation of acetylene) Ketene - propiolactone process AN hydrolysis process		Propylene oxidation process (via acrolein)		

Fig. 6.29 Technological history of major industrial organic chemicals. (Ethylbenzene – Acrylic acid in 1950s – after 1990s)

Product	1950s	1960s	1970s	1980s	After 1990s
MMA				Isobutylene oxidation process (via methacrolein) t-Butanol oxidation process (via methacrolein) Ethylene raw material process	MGC process Direct meta process of isobutylene
Acetaldehyde	Hydroxylation of ethylene (Hoechst-Wacker process)				
Acetic acid	Oxygen oxidation process of naphtha	Oxygen oxidation of ethylene process acetaldehyde	Carbonylation process of methanol		Direct oxidation process of ethylene
Vinyl acetate	Acetic acid oxidation of ethylene (Hoechst-Wacker process)				
Vinyl chloride		Chlorine addition to ethylene, de-HCl process (EDC process) Acetylene-ethylene combination process	Oxychlorination process		
Phenol	Cumene process	Oxidation process of cyclohexane Benzoic acid process			
Adipic acid	Cyclohexane - cyclohexanol - nitric acid oxidation process				
Caprolactam	Cyclohexane - Anon - oxime - Beckmann rearrangement process Peracetic acid process (cyclohexane - Anon - caprolactone - lactam)	Photonitrosation process (cyclohexane - oxime hydrochloride - Beckmann rearrangement) Cyclohexane - nitric acid nitration - oxime hydrogen reduction and rearrangement process			Cyclohexane - Anon - ammoximation - gas phase Beckmann rearrangement process
Terephthalic acid	Two-stage nitric acid oxidation process of PX Air oxidation and nitric acid oxidation process of PX The 1st Henkel process (o-phthalic acid isomerization) DMT process Amoco - mid-century process	The 2nd Henkel process (benzoic acid disproportionation)			
Phthalic anhydride		Catalytic oxidation process of o-xylene			
Maleic anhydride		Catalytic oxidation process of butylene	Catalytic oxidation process of n-butane		

Fig. 6.29 Technological history of major industrial organic chemicals. (MMA – Maleic anhydride in 1950s – after 1990s)

Technology	Before 1900	1900s	1910s	1920s	1930s
Utilization of natural polymer	Celluloid Nitrification cotton process rayon	Viscose process rayon	(viscose) cellophane	Nitrocellulose lacquer Acetate fiber, coating	
Synthetic polymer **(Addition condensation)**			Phenolic resin	Urea resin	Melamine resin
(condensation polymerization, thermosetting)					
(condensation polymerization, thermal plasticity)					Nylon
(Oxidative polymerization)	Dry oil paint			Alkyd resin	
(radical polymerization)				Vinyl acetate resin Vinyl chloride resin	Polystyrene PMMA LDPE Chloroprene rubber SBR NBR
(Ion polymerization)					
(Metathesis)					

Fig. 6.30 History of major polymer technology (before 1900 – 1930s)

Technology	1940s	1950s	1960s	1970s	1980s	After 1990s
Utilization of natural polymer		(acetate) Photographic film	(acetate) Cigarette filters			(acetate) Liquid crystal polarizing film
Synthetic polymer						
(Addition condensation) (condensation polymerization, thermosetting)	Unsaturated polyester Polyurethane Epoxy resin Silicone		Polyimide			
(condensation polymerization, thermal plasticity)		Polyester PET PET film Polycarbonate	PPO Polyurethane-type thermoplastic rubber Polysulfone Meta-aromatic aramid	PBT PES Para-aromatic aramid	PEEK Polyetherimide Liquid crystal polymer	
(Oxidative polymerization)			PPO			
(radical polymerization)	Vinylon AS resin ABS resin Fluororesin	Acrylic				
(Ion polymerization)	Butyl rubber	Low-pressure process HDPE Medium-pressure process HDPE Polyacetal Polypropylene	Styrene-type thermoplastic rubber EPDM rubber Polyisoprene rubber cis-1,4-Butadiene-based rubber	L-LDPE	Metallocene PE	(Post-metallocene PE)
(Metathesis)						COP

Fig. 6.30 History of major polymer technology (1940s – after 1990s)

Development of technologies using reactions to places other than olefin double bonds took considerably longer than the technologies using additions to olefin double bonds. These technologies are all catalytic reactions. Allyl chloride was made from propylene in the 1940s, followed by the Hoechst-Wacker process (acetaldehyde from ethylene) in the 1950s, vinyl acetate by acetoxylation of ethylene, acrylonitrile by ammoxidation of propylene and maleic anhydride by oxidation of butylene in the 1960s, acrolein and acrylic acid by direct oxidation of propylene in the 1970s, MMA by oxidation of isobutylene in the 1980s, and so on.

In the 1920s, production of vinyl chloride started with the formation of EDC by an addition reaction of chlorine to ethylene, followed by dehydrogenation with an alkali. However, due to the fact that this process wasted hydrogen chloride, it came to be replaced by the acetylene process. In the 1950s, the EDC process revived as a result of a cheap supply of ethylene and the hydrogen chloride being collected by thermal cracking of EDC. However, this process was really only applicable when there was a consumer with a demand for the collected hydrogen chloride. One such consumer was the ethylene/acetylene coproduction process, in which hydrogen chloride was added to acetylene. For this purpose, even processes for manufacturing basic petrochemicals (co-production of acetylene and ethylene) by flame cracking of naphtha and high-temperature steam cracking of crude oil were developed. In the 1970s, the ethylene oxychlorination process was developed, and vinyl chloride was subsequently only produced using the

EDC process combined with the oxychlorination process.

Although some manufacturing technologies for aromatic industrial organic chemicals had long been used in coal tar chemistry, most of the petrochemical technologies in the narrow sense were developed between the 1950s and 1960s, coming after the manufacturing processes for olefins. In the 1950s, phenol became a petrochemical product, with the development of the cumeme process superceding the existing coal chemistry technology., The cyclohexane process was also developed in the 1950s for manufacture of adipic acid and caprolactam, replacing the phenol process, which had been used since the coal chemistry period. Manufacture of pthalic anhydride by catalytic oxidation of o-xylene was developed in the late 1960s. This technology superceded the oxidation of naphthalene from coal tar. It may be said that terephthalic acid as a raw material for polyester is an industrial organic chemical that was developed between the periods of coal chemistry and petroleum chemistry, because it has been in demand since petroleum chemistry became widespread to Europe and Japan in the 1950s. Accordingly, in the 1950s, coal chemistry technologies (first and second Henkel processes) and petrochemistry technologies (air oxidation/nitric acid oxidation of p-xylene, DMT process and Amoco process) were both developed one after another, competing with each other.

Of the technologies for manufacturing industrial organic chemicals with syngas, only the manufacture of acetic acid by carbonylation of methanol, developed in the 1970s, may be classified as a petrochemical technology in the narrow sense. The bases for production technologies for methanol, formaldehyde, etc. had already formed in the coal chemistry period.

As mentioned above, among the technologies for manufacturing industrial organic chemicals by petroleum chemistry in the narrow sense, addition reaction to the double bond of olefins began with stoichiometric reactions in the 1920s, later replaced by catalytic reactions in many cases from the 1930s onwards. Reaction processes to places other than olefin double bonds were developed in the 1950s and have since then been extending the range of olefin chemistry. Manufacturing technologies for aromatic industrial organic chemicals by petrochemistry bore fruit based on coal tar chemistry in the 1950s. However, the main technologies for many products including caprolactam and adipic acid, were established during the period of coal chemistry.

(3) Polymer technology

The history of polymer technologies has been mentioned in some detail in Section 6.1.3. It is summarized in Fig. 6.30. In the 1940s, 1920s petrochemistry combined with polymerization for the first time in the United States; at that time, large amounts of synthetic rubber (SBR) were being produced from butadiene in line with United States national policy. This triggered dramatic developments in petroleum chemistry from the 1950s onwards. However, perhaps unexpectedly, the basic technology of sequential polymerization was formed in the coal chemistry era before the 1940s, as shown in Fig. 6.30. Nevertheless, sequential polymerization has also created many new polymers in petrochemistry since the 1960s, such as the recently developed functional polymers.

Meanwhile, in chain polymerization, radical polymerization has produced many significant polymers (polyvinyl chloride, vinyl acetate resin, poly (methyl methacrylate), polystyrene, chloroprene rubber, SBR, NBR, ABS resin, acrylic fiber, LDPE, etc.). The main monomers for radical polymerization were produced and industrialized in coal chemistry (acetylene chemistry and coal tar chemistry) and fermentation chemistry (ethanol). These basic technologies were established independently of petrochemistry. In the 1940s, ionic polymerization produced butyl rubber, BR, etc. mainly from petrochemical raw materials.

As mentioned above, monomers for many polymerization technologies were developed and industrialized independently of petrochemistry. In contrast, coordination anionic polymerization was only created in petrochemistry in the 1950s. This technology subsequently made a substantial contribution to the dramatic development of petrochemistry. As this technology is already described in detail in Section 6.1.3 (1) 4), any further explanation of it is omitted here.

(4) Essence of petrochemical technology

As discussed above, when reviewing the history of petrochemical technology in the narrow sense, the petrochemical technologies that have played the most important role in the technological development of petrochemistry since it was created to the present can be considered to be olefin manufacturing processes for basic petrochemicals, olefin chemistry for industrial organic chemicals and olefin polymerization processes for polymers

Of the processes for manufacturing basic petrochemicals (Fig. 6.2), the technologies for manufacturing syngas and aromatic hydrocarbons supplement the technologies for manufacturing olefins. Syngas manufacturing technologies were essentially established in coal chemistry; the same is true of aromatic hydrocarbon technology in petroleum refining technologies. These prior technologies flowed over into petrochemistry.

Of the manufacturing technologies for industrial organic chemicals (Fig. 6.16), aromatic hydrocarbon chemistry, cycloparaffin chemistry, C1 chemistry and other organic synthetic chemistry supplement olefin chemistry. Aromatic hydrocarbon chemistry, C1 chemistry and other types of organic synthetic chemistry were developed in coal chemistry or fermentation chemistry and then flowed over into petrochemistry. Cycloparaffin chemistry came into being in petrochemistry but has not flourished, other than for cyclohexane.

Of the polymer manufacturing technologies (Figs. 6.22 and 6.24), coordination anionic polymerization, included in ionic polymerization of chain polymerization, has played a central role. On the olefin polymerization technologies, radical polymerization (LDPE) in the 1930s, anionic and cationic polymerization (polybutadiene and butyl rubber) in the 1940s and metal oxide polymerization (HDPE) were developed. Since the 1950s, coordination anionic polymerization has been a main stream of the technological development of polymers. Sequential polymerization and radical polymerization technology, whose foundation was already laid before the creation of petrochemistry, flowed over into petrochemistry, thus supplementing the technologies for manufacturing polymers in petrochemistry. However, the importance of sequential polymerization revived from the 1980s onwards, because petrochemistry began aiming towards functional chemistry.

6.3.2 Epoch-making petrochemical technology

Table 6.4 summarizes the epoch-making technologies that made substantial contributions to the progress of petrochemistry in its history of more than 100 years.

Table 6.4 Epoch-making technologies in the history of petrochemistry

Year	Technology
1920	Steam cracking of ethane
1930	Ethylene oxide by silver catalyst
1940	Steam cracking and product separation process of naphtha
1950	Acetaldehyde by the Hoechst-Wacker process
1950	Ammoxidation process for acrylonitrile
1950	Ziegler-Natta catalyst
1960	Utilization of zeolite ZSM-5 (ethylbenzene, p-xylene, etc.)
1960	Oxychlorination process for ethylene dichloride
1980	Metathesis reaction

It is well known that petrochemistry began with the production of isopropyl alcohol by the sulfuric acid process from waste gas obtained by thermal cracking of heavy oil in 1920. However, this process is only part of the organic synthetic processes that have been accumulated since the 19th century, because thermal cracking of heavy oil is a petroleum refining process for producing gasoline, and because the sulfuric acid process is a stoichiometric reaction using propylene and sulfuric acid. Therefore, it cannot be classified as an epoch-making petrochemical process. It is not well known that the steam cracking of ethane separated from natural gas was also industrialized in 1920. This process, however, can be said to be the first epoch-making technology in petrochemistry, because it subsequently played a very important role in the petrochemical industry, due to the fact that its main purpose was the production of ethylene as a raw material for chemicals, and the fact that a decrease of partial pressure by addition of steam was a versatile technology that was applicable to the production of other petrochemicals. Nevertheless, the process for steam cracking of naphtha and separation of products developed in the 1940s was still important, because it laid the foundation for the creation of petrochemistry in Europe and Japan in the 1950s.

Production technology for ethylene oxide in the presence of a silver catalyst was invented in France in the early 1930s and industrialized in the late 1930s. This technology was the first to be industrialized using a solid-supported catalyst in the history of petrochemistry. It is also very significant that the reaction associated with high risk of explosion, in which ethylene was mixed with oxygen or air to directly synthesize ethylene oxide, was successfully industrialized early in the history of petrochemistry.

Production technology for acetaldehyde by the Hoechst-Wacker process and production technology for acrylonitrile by ammoxidation in the 1950s and production technology for EDC by oxychlorination process in the 1960s markedly widened the range of olefin chemistry. These were epoch-making technologies, because they provided petrochemistry with a basis for completely dominating coal chemistry. In the 1980s, the metathesis reaction was developed, following on from the above three types of olefin chemistry. It, too, extended the range of olefin chemistry.

In the 1950s, the Ziegler-Natta catalyst was developed in the period of petrochemistry. This catalyst became a starting point for coordination anionic polymerization, which is still making advances to this day. It was also epoch-making in that it produced large-scale petrochemical products (polyethylene, PP and various synthetic rubbers).

The zeolite ZSM-5 process developed in the 1960s is a solid catalyst/adsorptive separation technology that utilizes steric structure-controlled empty holes. This technology was widely used in various areas of petrochemistry and, moreover, it became a starting point for the utilization of steric structure-controlled empty holes other than those of ZSM-5.

6.4 Japanese petrochemical technology

This section discusses Japanese petrochemical technology in the context of the history of petrochemical technology worldwide. Currently, Japanese companies are leading the world in the development of some petrochemical technologies, including technology utilizing C4 olefins, post-metallocene catalysts and paraffin chemicals. Japan's new initiatives in functional chemistry are also dramatically changing the existing concepts of petrochemistry.

6.4.1 The history of Japanese petrochemical technology

Prior to petrochemistry, Japan already had a long history in developing mass-producing chemical industries, such as coal chemistry. Although these chemical industries were dealt a devastating blow by the Second World War, the technology was not lost. When adopting Western petrochemical technology in the 1950s, Japan drew on its existing technological expertise, quickly absorbing petrochemical technology and moving on to being an active player in the *Sturm und Drang* period of petrochemistry. This laid the foundation for Japanese companies to become frontrunners in functional chemistry from the 1980s onwards, and to spark new trends in petrochemical technology.

(1) The 1950s: Japanese petrochemistry launches on domestically-produced technology

As discussed in Section 5.3.3 (2), petrochemistry in Japan started in 1952 with the production of syngas and methanol by Japan Gas Chemical using natural gas from Niigata as a raw material. Methanol had been produced in Japan since the start of the 20th century by the wood retorting industry; syngas had been produced since the 1930s using coal as a raw material. Accordingly, Japan already had the technology to produce methanol from syngas since before the Second World War. The technology to produce syngas from natural gas had been developed through joint research between Japan Gas Chemical and Japan Gasoline (Table 6.5). Leading up to the early 1950s, there were a number of instances of Japanese companies using their own technology developed before and during the war to produce acetylene chemical products and coal tar chemical products, as shown in Table 6.5. The technology developed by Japan Gas Chemical was one such example.

Table 6.5 In-house technology of industrial organic chemicals and polymers developed after the Second World War and up to the first half of the 1950s

Year	Company	Product
1946	Toshiba Corporation Shonan, Yokahama Rubber	Start of production of acetylene-process vinyl chloride resin
1947	The Nippon Synthetic Chemical Industry	Production resumed on acetylene-process vinyl acetate (Start of production in 1936)
1948 to 1951	Tekkosha, Denki Kagaku Kogyo and others	Start of production of acetylene-process vinyl chloride resin
1950	Kurashiki Rayon	Start of production of polyvinyl alcohol and vinylon
1951	Toyo Rayon	Completion of a plant to produce nylon with a 5t daily production capacity
1951	Toagosei Chemical Industry	Completion of caprolactam synthesis technology
1952	Nippon Shokubai	Completion of maleic anhydride facility of benzene gas-phase oxidation process
1952	Japan Gas Chemical, Japan Gasoline	Completion of steam catalytic reforming technology of natural gas
1953	Nippon Shokubai	Start of anthraquinone production by anthracene gas-phase oxidation
1953	Kureha Chemical Industry	Start of production of vinylidene chloride resin

Source: Prepared from reference [5] and each company's homepage

Of course, not all such technology developments were necessarily successful. "On the Petroleum-Based Synthetic Chemical Industry," published by the Ministry of International Trade and Industry, Organic Division on June 1, 1951, noted the research by Japan Gas Chemical, as well as experiments by Gas Denko Bunkai to produce acetylene gas and hydrogen by arc cracking natural gas. It stated that there were plans to industrialize acetylene-process vinyl chloride and vinyl acetate based on this success. However, domestic technological development of the arc method ultimately never came to fruition.

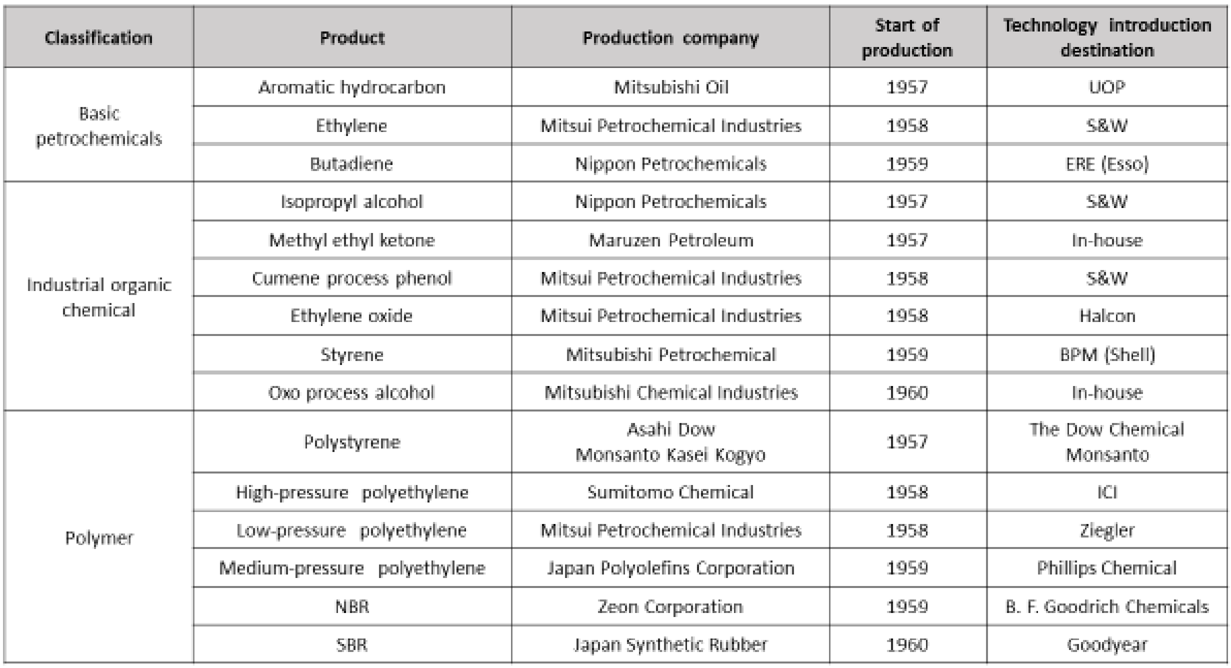
With oil refineries reaching a certain

level of development, as mentioned in Section 5.3.3 (3), Nippon Petro Chemicals produced isopropyl alcohol and acetone from petroleum waste-gas propylene in 1957, while Maruzen Petrochemical produced sec-butyl alcohol and MEK from n-butylene, also found in petroleum waste gas. This is generally regarded as the start of petrochemistry in Japan. While Nippon Petro Chemicals was using introduced technology, Maruzen Petrochemical had developed its own. We must not forget that Japanese petrochemistry did not start out on introduced technology alone, but with a wealth of independently-developed technology as well.

(2) The 1960s: The introduced technology rush and domestically-produced petrochemical technology

In the 1950s, Japan was on the receiving end of an influx of information about major petrochemical developments in the West, not only within the field of petrochemistry, but also in petrochemistry-related technology fields that were new to the pre-war chemical industries (chemical engineering, instrumentation and control technology, instrumental analysis and plastic molding, as discussed in Chapter 2). The Japanese chemical industry was shocked by the major technology gap with the West that had sprung up during the information blackout period in the Second World War. Japan started increasing its imports of PVC, polystyrene, polyethylene and other polymers. This presented a significant problem, given the foreign currency situation at the time. Accordingly, Japan immediately set about licensing the petrochemical and related technologies that were lacking in Japan, and aimed towards creating a petrochemical industry in Japan, starting with the steam-cracking of naphtha. The Japanese government pushed and supported this. As shown in Table 6.6, the vast majority of the petrochemical products initially produced by Japan in the last 1950s were achieved through introduced technology. Later, as the Japanese petrochemical industry began to become more established through more technology licensing from the West in the 1960s, the idea began to take hold in Japanese society that almost all petrochemical technology in Japan was introduced technology. Delegations of a number of Japanese chemical companies flocked to Italian company Montecatini, which developed PP, in the hope of establishing technology licenses; this is jokingly referred to as the “Monte visit.”

Table 6.6 The earliest stage of petrochemical products and technologies in Japan



Classification	Product	Production company	Start of production	Technology introduction destination
Basic petrochemicals	Aromatic hydrocarbon	Mitsubishi Oil	1957	UOP
	Ethylene	Mitsui Petrochemical Industries	1958	S&W
	Butadiene	Nippon Petrochemicals	1959	ERE (Esso)
Industrial organic chemical	Isopropyl alcohol	Nippon Petrochemicals	1957	S&W
	Methyl ethyl ketone	Maruzen Petroleum	1957	In-house
	Cumene process phenol	Mitsui Petrochemical Industries	1958	S&W
	Ethylene oxide	Mitsui Petrochemical Industries	1958	Halcon
	Styrene	Mitsubishi Petrochemical	1959	BPM (Shell)
	Oxo process alcohol	Mitsubishi Chemical Industries	1960	In-house
Polymer	Polystyrene	Asahi Dow Monsanto Kasei Kogyo	1957	The Dow Chemical Monsanto
	High-pressure polyethylene	Sumitomo Chemical	1958	ICI
	Low-pressure polyethylene	Mitsui Petrochemical Industries	1958	Ziegler
	Medium-pressure polyethylene	Japan Polyolefins Corporation	1959	Phillips Chemical
	NBR	Zeon Corporation	1959	B. F. Goodrich Chemicals
	SBR	Japan Synthetic Rubber	1960	Goodyear

Source: Prepared from reference [5]

However, as mentioned in Chapter 5, as

the United States petrochemical technology transferred to Europe in the 1950s, it blended with European chemical technology. Many significant petrochemical technologies had their origins in Europe, while the United States began to import these European technologies in return. From the 1950s onwards, petrochemical technology began to spread beyond borders, unlike the situation before the Second World War. This was part of the international spread of petrochemical technology; it was not necessary to humiliate itself for licensing. As a result, Japan’s introduced technology rush from the late 1950s to the early 1960s saw Japan opt for technology licensing instead of the time, costs and various risks involved in in-house development. One typical example is the licensing of nylon technology by Toyo Rayon (now Toray). Toray had started researching nylon before the war and started production in 1951 using its own in-house technology, as shown in Table 6.5. Prior to that, it had developed the market with products such as fishing lines and fish nets at the protoype stage, which boosted its business performance immediately after the war. Nevertheless, it outlaid significant capital and took the plunge into introduced technology. This was due to wanting to secure the market at an early stage using technologies that would develop the market for clothing applications, such as weaving and dyeing, as well as polymerization, spinning and other nylon production technologies; avoiding patent disputes with DuPont was also a factor.

There was one field of petrochemical technology in which Japan had absolutely no prior underlying experience: steam-cracking technology, developed from petroleum refining technology. There were similar situations in Europe; Japan was not the only place to heavily rely on introduced technology. However, Zeon and Kureha Chemical Industry developed and industrialized high temperature steam cracking for naphtha and crude oil in this very field, just as Europe was attempting crude oil cracking and naphtha catalytic cracking. The aim of this steam-cracking technology was to co-produce acetylene and ethylene and to produce vinyl chloride by the EDC process and the acetylene process at the same time.

In those early days of petrochemistry, when Japan was caught up in introduced technology, the industrialization of oxo alcohols by Mitsubishi Kasei in 1960 using its own technology is worth noting. This is said to have been the result of research undertaken with reference to the post-war PB Reports researched and published by the United States on wartime German science and technology.

As shown in Table 6.7, although technologies were developed in the West from the late 1950s to the early 1960s, Japan was often the first or among the first to industrialize them. In several cases, Japanese companies played a very significant role in finishing off industrial technologies for Western technological development companies. Examples of this include HDPE by Mitsui Petrochemical Industries, PP by Mitsui Chemicals, and acrylonitrile by Asahi Kasei. Each of these is a very significant field of technology in the global history of petrochemistry.

Table 6.7 Examples of world first or very early industrialization in Japan of petrochemical technology

Product	Technology	Industrial-ization company	Industrial-ization year
Low-pressure polyethylene	Ziegler process	Mitsui Petrochemical Industries	1958
Terephthalic acid	The 1st Henkel process	Kawasaki Kasei Chemicals	1958
Terephthalic acid	Mid-century process	Mitsui Petrochemical Industries	1958
Medium-pressure polyethylene	Standard process	Furukawa Kagaku Kogyo	1959
Polypropylene	Montedison process	Mitsui Chemicals	1962
Acrylonitrile	Sohio process	Asahi Kasei	1962
Naphtha steam cracking	Esso type furnace	Tonen Sekiyu Kagaku	1962
Terephthalic acid	The 2nd Henkel process	Mitsubishi Chemical Industries	1963
Acetone	Wacker process	Daikyowa Sekiyu	1964

		Kagaku	
Alfin rubber	Solution processSBR	Nippon Alfin Rubber	1970

Source: Prepared from reference [5]

Furthermore, as shown in Table 6.8, a number of significant petrochemical technologies were developed in Japan as early as the mid-1960s. Some of this technology was produced in Japan and exported to the West, such as the GPB process by Zeon. The GPB process has since been exported to 49 plants in 19 countries.

Table 6.8 Important petrochemical technology developed in Japan in the 1950s to the 1960s

Industrialization year	Product	Technology	Development company
1957	Methyl ethyl ketone	FCCwaste gas utilization	Maruzen Petroleum
1959	Ethylene oxide	Ethylene oxidation process	Nippon Shokubai
1960	p-Xylene	Circulation treatment process	Maruzen Petroleum, Resources Research Institute
1960	Oxoalcohol	Propylene oxo process	Mitsubishi Chemical Industries
1963	Caprolactam	PNC process	Toyo Rayon
1964	Vinyl chloride	Naphtha high temperature decomposition of Kureha process	Kureha Chemical Industry, Chiyoda Corporation
1964	Phthalonitrile	Ammoxidation process	Nippon Shokubai
1965	Polybutadiene	JSR process	Japan Synthetic Rubber, Bridgestone
1965	Butadiene	GPB process	Zeon Corporation
1966	Vinyl chloride	Oxychlorination process	Toyo Soda Manufacturing
1967	n-Paraffin	Urea adduct process	Nippon Mining
1967	Benzene	Dealkylation of MHCprocess	Mitsubishi Petrochemical
1967	Vinyl chloride	GPA process	Zeon Corporation
1968	Mixed xylene	m-Xylene extraction isomerization process	Japan Gas Chemical
1970	Acrylic acid ester	Propylene oxidation process	Nippon Shokubai
1970	Vinyl chloride	Crude oil high temperature decomposition of Kureha process	Kureha Chemical Industry

Source: Prepared from reference [5] and each company's homepage

In the late 1960s, a very large number of plants started up through domestically produced technology, as shown in Table 6.9. Surprisingly, within only 5–10 years of petrochemistry taking hold in Japan with introduced technology at its core, a large number of latecomer companies were entering the market with their own independent technology in every petrochemical product field. This also suggests that newcomers to the Japanese petrochemical market in the late 1950s were eager to industrialize their products through introduced technology and were first trying to take a firm hold of the market.

Table 6.9 Examples of industrialization by domestic technology in the second half of 1960s

Name of company	Product	Start of production
Daicel Chemical Industries	Alkylamine	1965
Denki Kagaku Kogyo	Polystyrene	1965*
Showa Denko K.K.	Isophthalonitrile	1966
Showa Denko K.K.	Xylylenediamine	1966
Mitsui Toatsu Chemical	Polystyrene	1966
Mitsui Petrochemical Industries	Polypropylene	1967
Daicel Chemical Industries	Acrolein	1967
Tokuyama Soda	Vinyl chloride by oxychlorination process	1967
Sumitomo Chemical	Meta-, para-cresol	1967
Toyo Soda Manufacturing	Ethyleneamine	1967
Mitsubishi Chemical Industries	Medium-pressure polyethylene	1968
Daicel Chemical Industries	ABS resin	1968
Showa Denko K.K.	Chlorinated polyethylene	1968
Mitsui Toatsu Chemical	Vinyl chloride by oxychlorination process	1968
Idemitsu Petrochemical	Polycarbonate	1968
Idemitsu Petrochemical	Polystyrene	1968
Nippon	Petroleum resin	1968

Petrochemicals		
Daicel Chemical Industries	Synthetic glycerin	1969
Showa Denko K.K.	Polypropylene	1969
Dainippon Ink	Polystyrene	1969*
Mitsubishi Petrochemical	Ethylene	1969*
Mitsubishi Chemical Industries	Maleic anhydride	1970
Mitsui Petrochemical Industries	EPR	1970
Mitsui Petrochemical Industries	Meta, paracresol	1970
Tokuyama Soda	Polypropylene	1970
Tokuyama Soda	Chloromethanes	1970
Sumitomo Chemical	High-pressure polyethylene	1970*
Asahi Kasei	Medium-pressure polyethylene	1970
Idemitsu Petrochemical	Styrene	1970
Denki Kagaku Kogyo	ABS resin	1970*

Note: The asterisk (*) denotes the technology development year.
Source: Prepared from reference [6]

Nevertheless, even at this time there were still some fields that were highly dependent on introduced technology. These were fields of technology that had been established in the 1920s–1940s, when the petrochemical industry only existed in the United States (steam cracking, LDPE, styrene, synthetic rubber SBR). This was the point of difference afforded by a history of technology accumulation. By contrast, the petrochemical technologies that had come about in the 1950s era of fused Western technology were successively being developed as domestically produced technology. These included HDPE, PP, styrenic polymers and oxychlorination process for vinyl chloride.

While Japan came in towards the end of the *Sturm und Drang* period of petrochemistry, it was just in time to imbibe the atmosphere of that era. Not only did it simply adopt technologies developed in the West, it also became an active player in the *Sturm und Drang* period. Japanese petrochemistry had the good fortune to start out in a completely different era from many developing nations from the 1970s onwards. [Footnote 6]

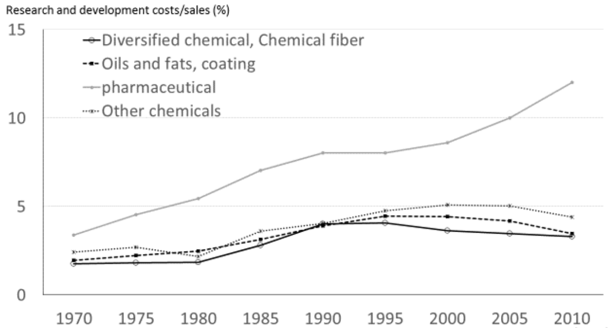
(3) The 1970s: Technologies developed in response to negative aspects emerging

With major developments taking place in the petrochemical industry in the 1970s, air pollution, water pollution and other negative aspects began to manifest. Overseas introduced technology could not be relied upon to combat air and water pollution; this was resolved within a relatively short space of time through domestically-produced technology. Japanese chemical companies were quick to respond, having already put high-pressure fat reduction technology, which produces straight-chain higher alcohols, to use since before the war; this technology was used to combat the issue of foam pollution from synthetic detergents in the mid-1960s. The petrochemical technology to extract n-paraffin, a starting material for obtaining higher alcohols from kerosene, was also developed by Nippon Mining in 1967 (Table 6.8).

Having caught up with the West in the 1970s, Japan was no longer lagging behind Western companies in its technological developments, even with the emergence of several negative aspects of petrochemistry from the 1970s onwards, as discussed in Section 5.5. Japan developed PCB processing, chlorofluorocarbon alternatives, processing for nitrous oxide produced in the course of making the raw materials for nylon and countermeasures for plastic waste issues.

(4) The 1980s: Increased research and development expenses for Japanese chemical companies

In the 1980s, Japanese chemical companies were increasingly very active in research and development, as shown in Fig. 6.31. Petrochemical companies are shown in Fig. 6.31 as “Diversified Chemicals / Chemical Fibers.” While petrochemistry had a lower R&D/sales ratio than other industries such as pharmaceuticals, the expense of research and development increased in the 1980s, and the R&D/sales ratio plateaued throughout the 1990s and 2000s.



Source: Ministry of Internal Affairs and Communications, science and technology research survey

Fig. 6.31 Change of the ratio of research and development expenses to sales of Japanese chemical companies.

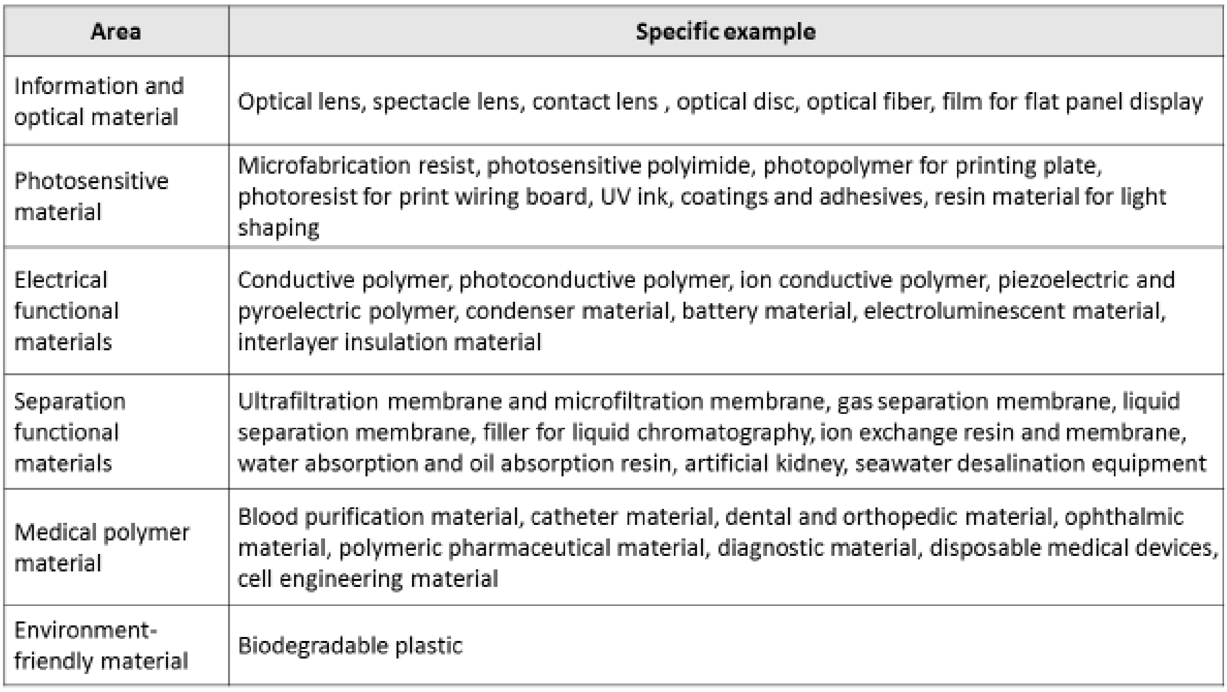
Research and development by petrochemical companies in the 1980s tended towards propylene/butylene chemistry, developing polymer structural materials, energy-conserving technologies and low-polluting technologies. At the same time, functional chemistry was being explored in developed nations, as the mass-produced petrochemical market was obviously well-developed. This resulted in the early appearance of engineering plastics utilizing polymer technology, semiconductor resists and photosensitive resins for print platemaking and other applications.

(5) From the 1990s onwards: Functional chemistry comes into full bloom

While functional polymer development continued to be at the core, the expansion into functional chemistry by Japanese chemical companies in the 1990s followed a different business model from the conventional petrochemistry in the West, namely, the development of functional chemical products through the integration of polymer processing. The expansion into polymer structural materials in the 1980s had still centered on technological developments focused on the properties of the material itself, such as heat-resistant or high-tensile engineering plastics, or superabsorbent polymers. However, the Japanese petrochemistry business model from the 1990s onwards went beyond the boundaries of petrochemistry (basic petrochemicals, industrial organic chemicals and polymers), the scope of the present study, even incorporating the parts/products stage of products made from polymers. Accordingly, the scope of research and development went beyond the boundaries of polymerization, even incorporating polymer processing technology and parts/products assessment technology, which generated much added value. Table 6.10 shows the functional polymer materials and functional chemical products focused on by Japanese petrochemical companies from the 1990s onwards. Japanese chemical companies lead the world in one of these fields, functional film, shown in Table 6.11. We cannot forget that petrochemical technology, particularly polymer technology, provided the basis for the technology to develop these functional chemistry products.

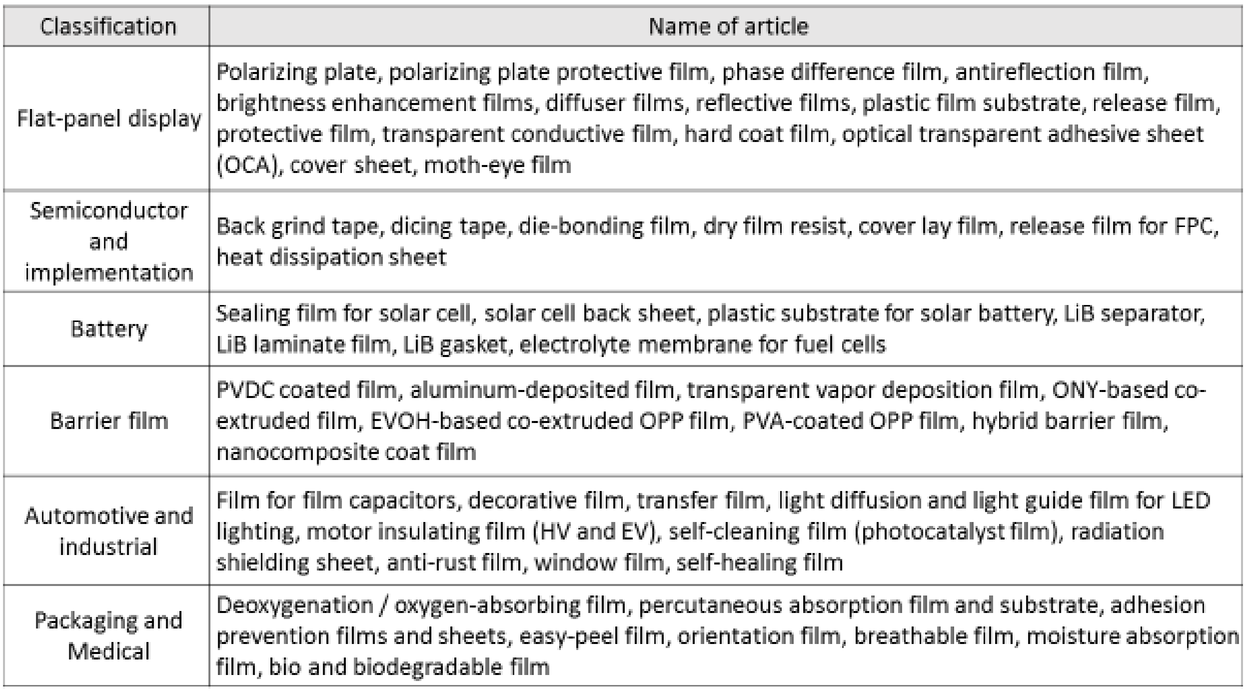
Meanwhile, Japanese petrochemical companies have also been markedly active in the fields of petrochemistry that fall within the scope of this study, even while many Western companies have been withdrawing from petrochemistry. A number of Japanese companies have contributed to the new synthesis technology for acrylic acid and methacrylic acid. This is the field of olefin chemistry, hydrocarbons with three or more carbon atoms and paraffin chemistry. Japanese companies have also played a key role worldwide in the development of post-metallocene catalysts.

Table 6.10 Functional polymer materials and molding products developed since the 1990s



Area	Specific example
Information and optical material	Optical lens, spectacle lens, contact lens , optical disc, optical fiber, film for flat panel display
Photosensitive material	Microfabrication resist, photosensitive polyimide, photopolymer for printing plate, photoresist for print wiring board, UV ink, coatings and adhesives, resin material for light shaping
Electrical functional materials	Conductive polymer, photoconductive polymer, ion conductive polymer, piezoelectric and pyroelectric polymer, condenser material, battery material, electroluminescent material, interlayer insulation material
Separation functional materials	Ultrafiltration membrane and microfiltration membrane, gas separation membrane, liquid separation membrane, filler for liquid chromatography, ion exchange resin and membrane, water absorption and oil absorption resin, artificial kidney, seawater desalination equipment
Medical polymer material	Blood purification material, catheter material, dental and orthopedic material, ophthalmic material, polymeric pharmaceutical material, diagnostic material, disposable medical devices, cell engineering material
Environment-friendly material	Biodegradable plastic

Table 6.11 Functional film and its utilization area



Classification	Name of article
Flat-panel display	Polarizing plate, polarizing plate protective film, phase difference film, antireflection film, brightness enhancement films, diffuser films, reflective films, plastic film substrate, release film, protective film, transparent conductive film, hard coat film, optical transparent adhesive sheet (OCA), cover sheet, moth-eye film
Semiconductor and implementation	Back grind tape, dicing tape, die-bonding film, dry film resist, cover lay film, release film for FPC, heat dissipation sheet
Battery	Sealing film for solar cell, solar cell back sheet, plastic substrate for solar battery, LiB separator, LiB laminate film, LiB gasket, electrolyte membrane for fuel cells
Barrier film	PVDC coated film, aluminum-deposited film, transparent vapor deposition film, ONY-based co-extruded film, EVOH-based co-extruded OPP film, PVA-coated OPP film, hybrid barrier film, nanocomposite coat film
Automotive and industrial	Film for film capacitors, decorative film, transfer film, light diffusion and light guide film for LED lighting, motor insulating film (HV and EV), self-cleaning film (photocatalyst film), radiation shielding sheet, anti-rust film, window film, self-healing film
Packaging and Medical	Deoxygenation / oxygen-absorbing film, percutaneous absorption film and substrate, adhesion prevention films and sheets, easy-peel film, orientation film, breathable film, moisture absorption film, bio and biodegradable film

6.4.2 World-class Japanese petrochemical technologies

Tables 6.7 and 6.8 show the petrochemical technologies developed by Japanese chemical companies in the 1950s–1960s. As a great many Japanese companies developed their own technology from the 1970s onwards, not all of them can be shown in these tables. Table 6.12 shows some of these independently-developed, world-class Japanese petrochemical technologies. We have already mentioned some of these: the oxo process by Mitsubishi Chemical (Section 5.4.2 (2) 1)); butadiene extraction by Zeon (Section 6.4.1 (2)); highly active catalysts for PP by Mitsui Chemicals (Section 6.1.3 (1) 4)); nitrite process by Ube Industries (Section 6.2.3); the others we shall mention briefly.

Table 6.12 World-class Japanese petrochemical technology

Industrial-ization year	Company	Technology

1959	Nippon Shokubai	Ethylene oxide production technology
1960	Mitsubishi Chemical	Oxo reaction technology
1962	Toray Industries	Caprolactam production technology of photonitrosation process
1965	Zeon Corporation	Butadiene extraction technology
1968	Mitsubishi Gas Chemical Company	m-Xylene separation, derivatives production technology
1970	Nippon Shokubai	Acrylic acid production technology of propylene direct oxidation process
1977	Mitsui Chemicals	High activity catalyst technology for polypropylene
1978	Sanyo Chemical	Superabsorbent polyacrylic acid resin production technology
1982	Mitsubishi Rayon and Nippon Shokubai	Methyl methacrylate production technology of isobutylene process
1984	Mitsubishi Rayon	Acrylamide production technology bio process
1992	Ube Industries	Oxidative carbonylation technology (nitrite technology)
2002	Asahi Kasei	Polycarbonate production technology of carbon dioxide as raw materials
2003	Sumitomo Chemical	Caprolactam production technology that produces no ammonium sulfate as a byproduct
2007	Asahi Kasei	Acrylonitrile production technology of propane process

Note: The company names are the current ones, not the names that were in use at the time of industrialization.

Nippon Shokubai successfully industrialized the production of phthalic anhydride by oxidation of naphthalene, maleic anhydride by the oxidation of benzene and anthraquinone by oxidation of anthracene in the coal chemistry era, which is around the Second World War. In 1959, the company developed its own technology to produce ethylene oxide by direct oxidation of ethylene, and industrialized this in an industrial complex in Kawasaki. Along with Mitsubishi Kasei's oxo process, this was one of the pinnacle achievements in early Japanese petrochemistry. The company also successfully industrialized the production of acrylic acid by direct oxidation of propylene in 1970, and MMA by direct oxidation of isobutylene in 1982. It has continued to pursue the development of oxidation technology.

Mitsubishi Gas Chemical was another Japanese petrochemical company like Nippon Shokubai that used its own technology to expand into unique areas of business. Its predecessor, Japan Gas Chemical, was the first to embark on petrochemistry in Japan with the industrial production of syngas and methanol from natural gas in 1952. Mitsubishi Gas Chemical was the first in the world to successfully isolate high-purity m-xylene from mixed xylenes in 1968, using its mastery of super-acid HF-BF_3. It has expanded into product categories that are unique worldwide: high-purity isophthalic acid (a raw material for PET denaturation and meta-aramid fiber) and m-xylenediamine (a raw material for aliphatic diisocyanates and MX nylon) from m-xylene.

There are two types of noteworthy caprolactam production technology: the photonitrosation method developed by Toray in 1962, and a method developed by Sumitomo Chemical in 2003 that produces no ammonium sulfate byproduct (developed from gas phase Beckmann rearrangement technology). Both technologies are truly notable in the history of caprolactam technology worldwide. Further details on these technologies are discussed in Section 6.1.2 (4).

The photonitrosation method developed by Toray is the only instance in the world of producing industrial organic chemicals using photoreaction. Similarly, Mitsubishi Rayon (Nitto Chemical Industry at the time, merged in 1998) developed a bio method for producing acrylamide through hydration of acrylonitrile using microorganisms as a catalyst. A little later, Mitsui Chemicals also developed a bio method for acrylamide production, industrializing it in Korea and licensing the technology to Finland in 2013 (see Section 3.4.3 (7)). While bio methods are used to produce small quantities of chemical products, such as amino acids, vitamins, pharmaceutical intermediates and optically active substances, there are no other instances worldwide of such methods being used in mass production other than in petrochemistry.

Asahi Kasei developed a non-phosgene polycarbonate production method using carbon dioxide as a raw material, and industrialized it through a joint venture in Taiwan in 2002. This technology was later exported to Korea, Russia, Saudi Arabia and other countries. Since it uses carbon dioxide as a raw material for the polymer and also does not use phosgene, it has received many awards in Japan as a low-emission technology, and also received an award from the American Chemical Society in 2014.

We have already discussed propane-based acrylonitrile production technique, also developed by Asahi Kasei and industrialized by a Korean subsidiary company, in Section 6.2.4. This is an innovative technology with the potential to break away from the conventional framework of olefin-focused petrochemistry. The propylene ammoxidation production method for acrylonitrile is a world-dominating technology held by British company BP. It was thought that BP would also develop a propane ammoxidation production method for acrylonitrile; Asahi Kasei took the world by surprise by doing it first. Section 6.3.2 introduced nine epoch-making petrochemical technologies. Asahi Kasei’s propane-based acrylonitrile production technology should be the tenth on this list, with the potential to open up a new field of petrochemistry, namely, paraffin chemistry. It was not included in Section 6.3.2, as its historical significance is not yet known.

6.5 Systematization of petrochemical technology and discussion

Figure 6.32 shows a systematization of petrochemical technology summarizing the contents of this report, including technology from the mass-producing chemical industries that had developed prior to the creation of petrochemistry.

As previously mentioned at length, petrochemical technology consists of three areas: basic petrochemicals, industrial organic chemicals and polymers. Industrial organic chemical technology has origins as early as the 18th century wood retorting industry; other industrial organic chemical technology dates back to coal tar chemistry in the late 19th century, carbide/acetylene chemistry in the 1910s and coke-based syngas chemistry in the 1920s. The wood retorting industry has disappeared, unable to compete with carbide/acetylene chemistry and syngas chemistry in the 1930s. While oleochemistry was created in the 1900s, it was in the 1920s that higher alcohol production technology (high-pressure hydrogen reduction technology for fats and oils) emerged, which would later have strong ties with petrochemistry; it was in the 1930s that production technology emerged for higher alcohol sulfuric acid ester salts, the first neutral detergent. Fermentation chemistry was created as a mass-producing chemical industry in the 1920s.

Polymer manufacturing technology also originated prior to petrochemistry; cellulose chemistry (celluloid, rayon, cellophane, acetate) was created between the end of the 19th century and the 1920s, using natural polymers in chemistry, and greatly flourished. Meanwhile, production technology for phenol resin, the first synthetic polymer, started in the 1910s through coal chemistry. A succession of polymers emerged in the 1920s and 1930s through radical polymerization; the monomers usedas the raw materials for these were produced by acetylene chemistry. In the 1940s, industrial production of LDPE by radical polymerization commenced. Ethylene, the raw material for LDPE, was mainly produced by dehydration of fermentation ethanol, as high purity was required.

By contrast, in the United States, industrial organic chemicals (IPA, EG, ethylene oxide) were being produced from basic petrochemicals (propylene from waste gas from heavy oil cracking, ethylene from steam cracking ethane) in the 1920s. This technology was purely petrochemical in origin. By the 1930s, petrochemistry had expanded to include various alcohols, tetraethyl lead and other products; however, petrochemistry only existed as a supply for industrial organic chemicals, alongside coal chemistry, fermentation chemistry and oleochemistry, according to the technological strengths of each industry. Petrochemistry as yet had no connection with polymers. Restrictions on raw materials also meant that petrochemical technology had yet to spread beyond the borders of the United States.

In the 1940s, the production of synthetic rubber SBR from butadiene was promoted strongly in the policies of the United States, triggering a connection between petrochemistry and polymers. Butadiene was being produced in the United States by butylene dehydrogenation; new developments in petrochemistry were beginning to bud. However, the United States butadiene production by butylene dehydration could not match that of fermentation ethanol; even for butadiene petrochemistry could not take the title on its own.

In the late 1940s, after the end of the Second World War, the U.S. petrochemical industry suddenly expanded significantly, driven by a raid growth in consumer demand for polymers. Production of PVC and polyvinyl acetate rapidly increased in acetylene chemistry, as did in nylon and phenol resin in coal tar chemistry, urea resin in syngas chemistry and LDPE and polystyrene in petrochemistry. The surging demand for polymers spread to Europe and then Japan in the 1950s. Naphtha steam-cracking technology was transferred from the United States, prompting the start of production of basic petrochemicals in Europe in the early 1950s, and in Japan in the late 1950s. An underlying factor to this may be the beginning of Middle Eastern crude oil being exported around the world.

Petrochemical technology, which had been developed in the United States since the 1920s, also spread to Europe in the 1950s and developed further, fusing with the chemical technologies there. This resulted in major developments in olefin chemistry and olefin polymerization technology in the 1950s and 1960s within the field of production technology for industrial organic chemicals and polymers. The quality and scale of steam cracking technology also increased rapidly during this time. In addition to olefins, the supply of aromatic hydrocarbons shifted from coal tar to cracked gasoline by naphtha steam-cracking and reformate by naphtha catalytic reforming. Industrial organic chemicals, which had once been produced by fermentation chemistry and acetylene chemistry, were almost exclusively switching to olefin chemistry. Even for polymers, as the range olefin polymer products expanded, almost all of the polymers produced by radical and sequential polymerization shifted to petrochemistry, where they had previously been made from monomers supplied by acetylene chemistry and coal tar chemistry. Consequently, monomers became cheaper, which in turn markedly increased the demand for polymers from radical and sequential polymerization. Conversely, cellulose chemistry quickly fell into decline at this time, under pressure from synthetic polymers.

The trends in the 1950s and 1960s show a near disappearance of acetylene chemistry due to the rise of olefin chemistry, while aromatic chemistry was incorporated into petrochemistry as the source of aromatic hydrocarbons changed almost completely from coal tar to petroleum. Coke-based syngas chemistry was also incorporated into petrochemistry due to the near complete change to natural gas and petroleum-based syngas. Oleochemistry fell under the rise of industrial organic chemicals (surfactants) produced by petrochemical technology. Cellulose chemistry fell under the rise of polymers produced by petrochemical technology, and the industry decreased significantly. In the field of fermentation chemistry, acetone and butanol fermentation disappeared as they were replaced by petrochemical technology, while ethanol fermentation also significantly reduced in scale, only surviving in fields in which the only demand is for fermentation products (vinegar feedstock, food preservatives, etc.).

Thus, by the 1970s, the industrial organic chemicals and polymers that had predated petrochemistry had all completely switched over to petrochemistry. Meanwhile, the era of high economic growth ended in the 1970s in Japan and in the West, and the rapid growth in demand for polymers also came to an end. The continuing emergence of innovative petrochemical technologies in the 1950s and 1960s also ended. Nevertheless, from the 1970s onwards, the explosive increase in polymer demand and the internationalization of petrochemistry spread from the more developed nations to the resource-rich nations of the Middle East, and then to Asia, and Central and South America, thus preventing the worldwide petrochemical industry from stagnating. New technological challenges arose in responding to energy conservation and environmental pollution issues, as well as meeting new demand from developed nations (sudden increased demand for propylene, functional chemistry). Technological development continued beyond the 1970s in response to these issues. Steady progress was also made in front-running petrochemical technologies, such as acetic acid through methanol carbonylation, metathesis reactions, metallocene catalysts and post-metallocene catalysts. The advent of paraffin chemistry also attracted some attention in contrast to conventional olefin-based petrochemical technology.

Due to the emergence of pollution problems from propylene tetramer synthetic detergents with poor biodegradability in the 1970s, synthetic detergents started being produced using higher alcohols from fats and oils. Oleochemistry revived and continued alongside petrochemistry. In the 2000s, there was a rapid increase in production of biodiesel oil made from fats and oils and methanol. Oleochemistry and petrochemistry continue to coexist in biodiesel oil production. Meanwhile, the 2000s also saw a rapid increase in fermentation ethanol from agricultural produce in the United States. This was put to use as a substitute for gasoline additive MTBE, which was regulated due to groundwater contamination issues. Production grew significantly in scope to match the production of ethylene in the United States. Fermentation chemistry revived to reclaim one small foothold over petrochemistry in response to global environmental issues. Thus, various environmental issues have had varying impacts on petrochemistry. However, petrochemistry can be expected to overcome these various environmental issues, chemical safety issues and energy conservation issues in future.

From the 1980s onwards, there has been a push for functional chemistry in Japan and other developed nations. For more than three decades, Japan has furthered its functional chemistry technology beyond the conventional bounds of petrochemistry, even extending it as far as polymer molding technology. Petrochemistry continues to grow and change beyond its conventional framework.

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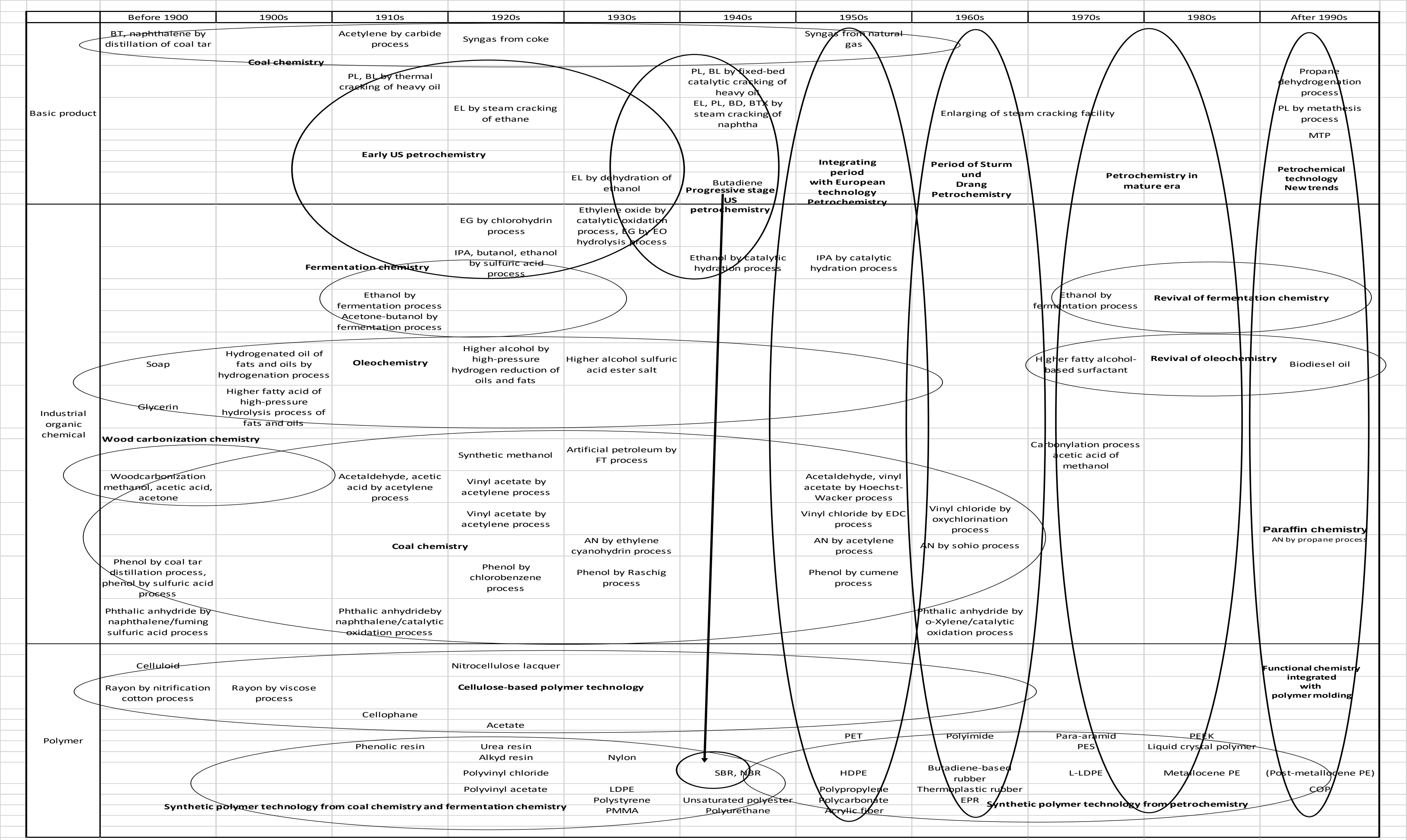

List of product abbreviations Ac: acetylene, EL: ethylene, PL: propylene, BL: butylene, B: benzene, T: toluene, X: xylene, AN: acrylonitrile

Fig. 6.32 Technology system of petrochemistry.

7 Conclusion

It has been 60 years since the establishment of the petrochemical industry in Japan. However, an “official history” of the Japanese petrochemical industry is more than a mere “Ten-year history” or “Twenty-year history” such as those given in bibliographic references 5 and 6 of Chapter 6. The “Thity-year history” in bibliographic reference 7 is too brief; the “Fifty years” in bibliographic reference 8 is little more than a chronology.

The main reason an “official history” is lacking is probably because the industry has trended from growth towards stagnation since the 1980s and has lost its appeal as an industry. An even more significant reason probably lies in the fact that petrochemistry has changed with the times, and even those in the industry cannot define exactly “what is petrochemistry?” In 2013, the Japan Petrochemical Industry Association invited submissions for a new name instead of “petrochemistry.” This is the extent to which we are unable to define “what is petrochemistry?”

Accordingly, we were at a loss, firstly in defining petrochemistry, and then how to narrow down the study area, taking into account the constraints of the investigation period. However, convinced that narrowing down the topic into a single area of petrochemistry (e.g. ethylene production technology) would not give adequate insight into the overarching picture of petrochemistry as a whole, we commenced researching this topic without narrowing down a specific study area. Rather than focusing solely on Japan, we also decided to aim the investigation as globally as possible and then position Japan within that. As a result, we have boldly gone beyond the normal bounds of petrochemistry in identifying trends in Japanese petrochemistry from the 1990s onwards, even incorporating polymer molding. This has been the path taken by Japanese petrochemical companies; they have not followed in the footsteps of petrochemistry overseas, but have branched out into functional chemistry while still remaining focused on petrochemistry.

Noted chemical companies in the West are continuing to withdraw from petrochemistry. British company ICI developed methyl methacrylate MMA and LDPE in the 1930s, polyester fiber in the 1940s, and engineering plastics PEEK and PES in the 1960s and 70s. Showing no signs of slowing in its technological prowess, it was the first to develop biodegradable plastics in the 1980s, and also developed chlorofluorocarbon alternatives in the 1990s. Despite these successes, ICI started withdrawing from the petrochemical industry in the 1990s and quickly lost its corporate identity. It sold off its operations in succession, and in 2008, the lauded company name disappeared through a merger. German company Hoechst AG, known for developing the Hoechst-Wacker process, HDPE and various kinds of engineering plastics, followed a similar path. The company ceased to exist once it lost the mainstay of its technological core, readily setting aside its core business and advocating non-petrochemistry. Many other major Western players in the industry have similarly abandoned the petrochemical industry, many of them attempting to expand into pharmaceuticals and agribusiness, with growing demand in developed nations, using biotechnology, rapidly developed since the 1970s, as their new technological axis. However, in many cases they have later felt on looking back that they have lost their former vitality and development potential. Meanwhile, the companies that have explored new areas of technology while remaining focused on petrochemistry have seen steady progress.

Japanese petrochemical companies have frequently been criticized for not having the same dynamic management as their counterparts in the West. However, their operations, while not showy, are solid and steady, and they have expanded into functional chemistry without losing their core focus on petrochemistry.

This report has intentionally focused within the realms of petrochemistry, on basic petrochemicals, industrial organic chemicals and polymers, and avoided delving too deeply into functional chemistry. However, it is interesting to note the number of new trends in petrochemistry since the 1990s, even within that scope. We have now reached the plateauing of petrochemical technology that we spoke about in the 1970s, and are on the verge of breaking through into a new stage. It is worth noting that Japanese petrochemical companies have played a major role in these trends.

Since Japanese petrochemistry has long lacked an “official history,” its history has not been recorded. Consequently, this survey report makes no attempt to summarize the collective opinions of the Japanese petrochemical industry; it is simply an “unofficial history” (privately composed history) written at will by the author as an individual. Given the present situation where there is not even a consensus on “what is petrochemistry?” there will of course be many counterarguments to the “unofficial history” presented by the author. However, this serves as an opportunity to start people thinking about the history of petrochemistry again. History does not simply end with recording the past; it provides guidelines for the future. The hope is that this survey report will to some extent serve in such a role.

Finally, the author would like to express heartfelt thanks to those who made this research opportunity possible, to the many people who cooperated in this study and to those who shared their valuable insights.

Location Confirmation of Historical Technology Resource Items from the Petrochemical Industry (including mass-produced chemical product items predating petrochemistry)

No.	Name	Format	Location, etc.	Place	Date of manufacture	Manufacturer	Reason for selection
1	Rayon research materials from the Former Yonezawa Higher Technical School (prototype, glass nozzle, wooden implements)	On display	Prof. Itsuzo Hata Memorial Room, Main Building, Former Yonezawa Higher Technical School	Faculty of Engineering, Yamagata University, Yonezawa, Yamagata	1913	Prof. Itsuzo Hata	Itsuzo Hata produced the first successful rayon prototype in Japan. A rayon factory was set up in Yonezawa using this technology, eventually leading to present-day Teijin. These items were discovered when the old research building was being demolished.
2	Rayon thread, rayon ribbon straw	On display	Prof. Itsuzo Hata Memorial Room, Main Building, Former Yonezawa Higher Technical School	Faculty of Engineering, Yamagata University, Yonezawa, Yamagata	1924-1930	Imperial Artificial Silk Co., Ltd.	Rayon thread and rayon ribbon straw manufactured during the period of stable operation of the Imperial Artificial Silk Yonezawa Plant (1916-1934). One of the few instances of early mass-produced products being kept.
3	High-pressure methanol synthesis catalyst KMA	In storage	Clariant Catalysts Toyama Plant	Toyama, Toyama	1989	Toyo CCI Co., Ltd.	Methanol synthesis research started at the Temporary Nitrogenous Fertilizer Laboratory in 1925. A catalyst production method was patented in 1927; Toyo Gosei successfully industrialized methanol synthesis in 1933 in Shimonoseki, Yamaguchi. Later, this catalyst was also sold to other Japanese companies and was used in the same form and composition up until 1989.
4	Celluloid compression tester	In storage	Daicel Corporation Himeji Production Sector Aboshi Plant	Himeji, Hyogo	1954	Dainippon Celluloid Co., Ltd.	Celluloid compression is a process whereby cellulose nitrate and camphor are mixed and then finished into blocks. While machines 1 and 2 were German-built and purchased in 1919, this is machine 3, the first domestically-produced machine.

5	Fermentation ethanol mash distillation column	In storage	Japan Alcohol Corporation Izumi Factory	Izui, Kagoshima	1938	State-run Izumi Alcohol Plant	A mash distillation column from the second state-run alcohol plant to start operating in Japan. Despite being damaged in an air raid in August 1945, it was rebuilt and remained in use until 1997.
6	Fermentation ethanol distillation column plates	In storage	Japan Alcohol Corporation Iwata Factory	Iwata, Shizuoka	1939	State-run Iwata Alcohol Plant	The Iwata Plant was the sixth of Japan's 13 state-run alcohol plants to start operating. These plates are part of a distillation column plate and a rectifying column or dehydrating column plate.
7	Fischer-Tropsch artificial petroleum synthesis catalyst and prototype	In storage	Institute for Chemical Research, Kyoto University	Uji, Kyoto	1927-1938	Institute for Chemical Research, Kyoto University	Prof. Genitsu Kita's laboratory at Kyoto University started research on artificial petroleum synthesis from syngas in 1927, the year after the F-T process was discovered in Germany. Iron-based catalysts as a substitute for the existing cobalt-based catalysts were discovered in 1937. These items are a catalyst and a prototype.
8	Fischer-Tropsch artificial petroleum product industrialization resource	In storage	Takigawa Local Museum	Takigawa, Hokkaido	1942-1945	Hokkaido Artificial Petroleum Co., Ltd.	Artificial petroleum product produced at one of the large-scale F-T process artificial petroleum factories established through state policy.
9	Raw material feed pump from Japan's first ethylene plant	In storage	Mitsui Chemicals Iwakuni Otake Factory	Iwakuni, Yamaguchi	1958	Mitsui Petrochemical Industries Co., Ltd.	A raw material feed pump from the first naphtha steam-cracking ethylene plant to start operating in Japan. It operated from 1958 to 1971.
10	Ethylene plant gas-driven compressor power piston	In storage	Mitsui Chemicals Iwakuni Otake Factory	Iwakuni, Yamaguchi	1962	Mitsui Petrochemical Industries Co., Ltd.	A gas-driven compressor power piston, arguably the central component, from the second ethylene plant at the Iwakuni Plant. Adopted as a state-of-the-art piece of technology at the time, it could handle a wide range of loads and fuel gas compositions.

11	Japan’s first low-pressure HDPE polymerization reactor	In storage	Mitsui Chemicals Iwakuni Otake Factory	Iwakuni, Yamaguchi	1958	Mitsui Petrochemical Industries Co., Ltd.	Even on global standards, this is a very early polymerization machine for producing low-pressure polyethylene, invented by Prof. Ziegler of Germany in 1955. This operated from 1958 to 1989.
12	High-pressure LDPE pilot test data	In storage	Institute for Chemical Research, Kyoto University	Uji, Kyoto	1951-1954	Institute for Chemical Research, Kyoto University	Diagrams, photographs, experiment notes and internal reports from pilot tests for producing high-pressure polyethylene carried out after the war, based on small-scale wartime experiments.
13	Japan’s first high-pressure LDPE product	On display	Sumitomo Chemical Company Ehime Factory History Museum	Niihama, Ehime	1958	Sumitomo Chemical Co., Ltd.	Japan’s first full-scale industrial production of high-pressure polyethylene, using licenced technology from UK company ICI.

A list of abbreviations for the product names used in this document

Abbreviation	Name	Details
2,4-D	2,4-Dichlorophenoxyacetic acid	Herbicide (agricultural chemical)
ABS resin	Acrylonitrile-butadiene-styrene resin	Semi-general-purpose plastic
ACH	Acetone cyanohydrin	Organic intermediate
AE	Alkylethoxylate, alcohol ethoxylate	Nonionic surfactant
AES	Alkyl ether sulfate	Anionic surfactant
AOS	α-Olefin sulfonate	Anionic surfactant
AS	Alkyl sulfonates	Anionic surfactant
AS resin	Acrylonitrile-styrene resin	Semi-general-purpose plastic
BHC	Benzene hexachloride	Insecticide (pesticide)
BPA	Bisphenol A	Monomer
BR	Butadiene rubber	General-purpose synthetic rubber
CMC	Carboxymethyl cellulose	Dispersion stabilizer for food, binder, emulsifier
COP	Cyclic olefin polymer	Excellent plastic for optic use
CPP Film	Cast polypropylene film	Transparent packaging film
CR	Chloroprene rubber	Synthetic rubber outstanding in weather resistance
DBP	Dibutyl phthalate	Plasticizer
DDT	Didchlorodiphenyl-trichloroethane	Insecticide (pesticide, drug for public heath)
DMF	N,N-dimethylformamide	Polar solvent
DMSO	Dimethyl sulfoxide	Polar solvent
DMT	Dimethyl terephthalate	Monomer
DOP	Dioctyl phthalate	Plasticizer
EDC	Ethylene dichloride	Organic intermediate
EDTA	Ethylenediaminetetraacetic acid	Chelating agent
EG	Ethylene glycol	Monomer, antifreeze
EPDM	Ethylene propylene diene monomer rubber	Synthetic rubber
EPR	Ethylene-propylene rubber	Synthetic rubber
EVA	Ethylene-vinyl acetate copolymer	Plastic, adhesive
HDPE	High-density polyethylene	General-purpose plastic
HIPS	High impact polystyrene	General-purpose plastic

Abbreviation	Name	Details
HNBR	Hydrogenated nitrile rubber	Special synthetic rubber
IIR	Isobutylene isoprene rubber (butyl rubber)	Special synthetic rubber
IPA	Isopropyl alcohol	Solvent
IR	Isoprene rubber	General-purpose synthetic rubber
LAS	Linear alkylbenzenesulfonate	Anionic surfactant
LDPE	Low-density polyethylene	General-purpose plastic
L-LDPE	Linear low-density polyethylene	General-purpose plastic
MAO	Methylalumoxane	Component of polymerization catalysts
MDI	Methylene diphenyl diisocyanate	Monomer
MEK	Methyl ethyl ketone	Solvent
MMA	Methyl methacrylate	Monomer
MTBE	Methyl tertiary butyl ether	Gasoline additive
MVA	Monovinylacetylene	Organic intermediate
NBR	Nitrile rubber, acrylonitrile butadiene rubber	Special synthetic rubber
OPP film	Oriented polypropylene film	Transparent packaging film
PBT	Polybutylene terephthalate	General-purpose engineering plastic
PCB	Polychlorinated biphenyl	Heat transfer medium, solvent, insulating oil
PCP	Pentachlorophenol	Herbicide, disinfectant
PEEK	Polyether ether ketone	Super engineering plastic
PES	Polyether sulfone	Super engineering plastic
PET	Polyethylene terephthalate	Plastic, synthetic fiber
PP	Polypropylene	General-purpose plastic
PPE	Modified polyphenylene ether	General-purpose engineering plastic
PPO	Polyphenylene oxide	General-purpose engineering plastic
PPS	Polyphenylene sulfide	Super engineering plastic
PTA	High-purity terephthalic acid	Monomer
PTFE	Polytetrafluoroethylene (Teflon)	Plastic
PTMG	Polytetramethylene ether glycol	Monomer
SAN	Styrene acrylonitrile (same as AS resin)	General-purpose plastic
SBR	Styrene-butadiene rubber	General-purpose synthetic rubber

Abbreviation	Name	Details
SBS	Styrene-butadiene-styrene block copolymer	Thermoplastic elastomer
SIS	Styrene-isoprene-styrene block copolymer	Thermoplastic elastomer
TDI	Toluene diisocyanate	Monomer
THF	Tetrahydrofuran	Solvent, monomer
ULDPE	Ultralow-density polyethylene	Plastic
VLDPE	Very low-density polyethylene	Plastic

Note: The above names are not based on the IUPAC Nomenclature, but are usually used in the chemical industry.