Petrochemical Industry in Japan

Part. 2. Recent Trends of Production and Utilization of Aromatics in Japan*

Tozo Amemiya**, Etsuro Nakamura*** and Shohei Tanji****

Introductory

The production of aromatic hydrocarbons in Japan relied exclusively upon coal carbonization industry, as in European countries, for longer than half a century, and first in 1958 two companies commenced to produce petroleum aromatics. Since then, the role of petroleum aromatics continued to increase in importance and nowadays production from coal carbonization and from petroleum is almost equal. The increasing production rate of the latter is expected to overcome the former in coming years also.

The demand for aromatic hydrocarbons has massively increased for the production of intermediates for such synthetic high polymers as plastics, fibres and rubbers.

I. Production of Aromatics

1. Aromatics from coal carbonization

Coal carbonization has long been practised in Japan at iron foundries, gas works and chemical works, and accordingly it is usual that processing of coal tar, including light oil recovered from coal gas, and separation of useful tar components are carried out by those industries. Aromatics from coal carbonization were the main source of fine aromatic chemicals and solvents, before petroleum aromatics were industrialized in 1958. (Fig. 1)

It is characteristic of aromatics from coal carbonization that the benzene ratio in the BTX fraction is extremely high and moreover naphthalene is exclusively supplied from coke ovens.

As most gas works and chemical industries

Fig. 1. Production of aromatics from coal carbonization

have already changed their source of raw material from coal carbonization to petroleum cracking, only the new coke ovens to be erected to supply coke to the expanding iron industry will provide some supplementary sources of aromatics from coal.

2. Petroleum aromatics

The pioneers in producing petroleum aromatics in Japan were Mitsubishi Oil Co. and Mitsui Petrochemical Co. in 1958, and Maruzen Oil Co. in 1959. Two petroleum companies made aromatics from reformat and Mitsui Petrochem. Co. from both reformat and cracked naphtha byproduced at their ethylene-producing plant.

As shown in Fig. 2, the total production of petroleum aromatics has already surpassed that from coal carbonization, excepting that naphthalene is supplied from coke ovens only.

It is well known that the content of toluene and xylene in reformat is very high, but only one refinery, Asia Oil Co. at Yokohama, has erected a hydrodealkylation plant to transform toluene and xylene to benzene. Such processes have always been assumed uneconomical because of the high price of hydrogen in Japan; However the selective

* Received September 30, 1966.

** Govern. Ind. Development Lab., Hokkaido.

*** Resources Research Institute.

**** Japan Tar Ind. Assn.

Fig. 2. Share of petroleum aromatics in total aromatics

production¹⁾ of *p*-xylene from mixed xylene through the fractional crystallization process combined with the catalytic isomerizations of *o*- and *m*-xylene to *p*-xylene has been successfully industrialized since 1960.

Most Japanese refineries seem to prefer the production of aromatic motor fuel having high octane number to the separation of aromatics for chemical uses from reformat, while the petrochemical enterprises are going to increase their production of aromatics from cracked naphtha byproduced in ethylene production, which is, otherwise, returned to a refinery. Thus, the main portion of the future supply of aromatics must come from those sources in the petrochemical industry.

The production of naphthalene through hydrodealkylation of alkyl naphthalene was tested in pilot plants by two or three companies, and they abandoned their plans as uneconomical. Now, as the feed stock for phthalic acid plant naphthalene as well as *o*-xylene, home-made or imported from abroad, can be used.

Some polycarboxylic acids derived from such polymethylbenzenes as mesitylene, pseudocumene and durene are promising intermediates of plastics, and recent analytical data²⁾ presents the latent sources for those

polyalkylbenzenes.

II. Utilization of Aromatics

1. Benzene

The consumption of benzene in the last decade is detailed in Fig. 3. In 1955 intermediates for dyestuff, etc. and phenol were

Fig. 3. Consumption of benzene

two main derivatives from benzene, but since about 1958 such derivatives as styrene, cyclohexane and maleic anhydride, which are raw materials of synthetic plastics, fibres and rubbers as like as phenol, have become more important. Development of these derivatives is at the same pace as petrochemical industries in Japan.

2. Toluene

The consumption of toluene in the past ten years is shown in Fig. 4. Most toluene has

Fig. 4. Consumption of toluene

been used as solvent, the remainder being transformed to derivatives for dyestuff, etc. Toluenediisocyanate and terephthalic acid are two newcomers among the derivatives of toluene, and the development of the latter is

more rapid than the former. The conversion of toluene to benzene is not regarded as having much merit because of the relatively high cost of hydrogen in Japan and there is no market for toluene as the blending stock of high octane gasoline.

3. Xylene

Xylene had been mostly used as solvents before *p*-xylene was separated from mixed xylene by two companies in 1960, and now 51% of the total production is used as solvent and 36% as *p*-xylene stock, as shown in Fig. 5.

Fig. 5. Consumption of xylene

Production of *p*-xylene is planned by two or three companies beside the present two, so the *p*-xylene percentage must rise up in the near future. Dealkylation of xylene to benzene or its use in gasoline blending has been generally unattractive in Japan.

4. Naphthalene

More than 80% of total naphthalene, exclusively supplied from coal carbonization, is consumed for production of phthalic anhydride, which is in turn used as an intermediate of plasticizers, terephthalic acid, etc. (Fig. 6).

Fig. 6. Consumption of naphthalene

III. Future Demand and Supply

The estimated demands of benzene, toluene and xylene in the coming five years are shown in Fig. 7, 8 and 9 respectively.

Among the derivatives of benzene, styrene and cyclohexane are to be the most important, the former as raw material for synthetic rubber and plastics, and the latter as the intermediate for caprolactum.

The large portion of toluene will still be used as solvents, and among its derivatives

Fig. 7. Demand of benzene*

Fig. 8. Demand of toluene*

Fig. 9. Demand of xylene*

terephthalic acid is becoming the most important.

Mixed xylene is mostly used as various solvents at present, but the selective production of *p*-xylene will take the largest percentage, that is about 55% in 1970.

Summing up the estimated demands of BTX in 1970, it amounts to 1.5 million tons. It is hoped that the total demand can be met with home-made aromatics. Cracked gasolines byproduced at ethylene-producing plants are expected to be the most reliable sources for petroleum aromatics, and the im-

* Estimated by Japan Tar Ind. Assocn. & Petrochem. Ind. Assocn. in 1966

port, mostly from U.S.A., will fill the temporary gap between demand and supply in the meanwhile.

IV. Technical Characteristics in Utilization of Aromatics

Such technical processes as solvent extraction, hydrosulfurization and reforming, which are applied for producing aromatics from petroleum or coal tar, have usually been imported from U.S.A. or West Germany. But there are several technical procedures for processing aromatic hydrocarbons chemically, which have been partly improved or wholly developed by Japanese technicians and successfully industrialized.

1. Photo-nitrosation of cyclohexane

Toyo Rayon Co. which industrialized Nylon 66 before World War II have recently developed their own photo-nitrosation process³⁾⁻⁶⁾ for synthesizing caprolactum from cyclohexane. In the process, cyclohexanone oxime can be derived directly from cyclohexane instead of the classical two or three step processes, and then transformed to the lactum.

The process was successfully applied to a 60 ton/day plant in 1963, and Toyo Rayon intend to revamp all their plants to the above process in the near future, it is reported.

Cyclohexane is produced in Japan by three or more companies with their own respective techniques.

2. Terephthalic acid from toluene

The process for simultaneously synthesizing terephthalic acid and phthalic anhydride via the corresponding chloromethyl derivatives from toluene is known as the Groschinsky process of West Germany, but no industrial know-how had ever been secured.

In 1966, Toyo Koatsu Industries, Inc. finished the first successful commercial 23 ton/day capacity TPA plant. The process may serve

to utilize cheap and abundant toluene from petroleum, it is expected.

3. Terephthalic acid from phthalic or benzoic acid

The Henkel process by which potassium phthalate or benzoate could be changed into the terephthalate at high temperature under high pressure in the presence of Cd salt, etc. was invented fundamentally in West Germany and developed commercially by three Japanese industries. The process contained many difficult engineering problems for the fact that solid materials must be forced to react at high temperature under high pressure. Kawasaki Kasei Co. in 1958 and Teijin Co. in 1959, both succeeded to operate their commercial plants to transform pot. phthalate to pot. terephthalate. Their present plant capacities are 30 ton/day and 55 ton/day respectively.

Recently, Mitsubishi Kasei Co. finished the disproportionation technique of pot. benzoate to pot. terephthalate and benzene. Their plant capacity is 60 ton/day.

These processes serve to supply the raw material for polyester fibre production.

4. Selective production of *p*-xylene

p-Xylene is one of the most suitable raw materials for terephthalic acid which in turn is the building material of polyester fibre. The recycle process^{1,7,8)} for selective production of *p*-xylene from mixed xylene has been successfully industrialized in Japan since 1960. The process is a combination of two stages, crystallization of *p*-xylene and isomerization of *m*- or *o*-xylene in the mother liquor to *p*-xylene, while ethylbenzene is cracked into benzene and stripped out. Thus,

Table 1. Capacities of terephthalic acid plants in Japan (1966)

Company	Location	Starting material	Process	Operation from	Capacity (TPA t/D)
Mitsui Petrochemical	Iwakuni	<i>p</i> -xylene	Mid-Century	1958	155
Maruzen Oil	Matsuyama	"	"	1960	60
Teijin-Hercules	Matsuyama	"	Witten	1963	76
Kurare-Yuka	Yokkaichi	"	Mid-Century	1967	40*
Mitsubishi Kasei	Kurosaki	"	"	1967	60*
Kawasaki Kasei	Kawasaki	phthalic acid	Henkel	1958	30
Teijin	Matsuyama	"	"	1959	55
Mitsubishi Kasei	Kurosaki	benzoic acid	"	1964	60
Toyo Koatsu	Sakai	toluene	Grosinsky	1966	23

* designed capacity

the yield of *p*-xylene rise up as high as 60–80%, compared with 12–13% in a simple crystallization process. The isomerization can be performed under atmospheric pressure in the presence of silica-alumina catalyst.

The process was studied with a pilot plant at Resources Research Institute and industrially applied by Maruzen Oil Co. at Matsuyama in 1960. Another Japanese company and a Bulgarian company have recently decided to adopt the same process.

5. Competition of various processes for terephthalic acid

Polyester fibre is one of the main products of the synthetic fibre industry in Japan. The total capacity of present two producers, Toyo Rayon and Teijin, was 202 ton/day in 1965, and two or three more companies have plans to participate in this field. Thus, the demand for terephthalic acid, the building material of polyester, is increasing year after year.

There is no demand for toluene and xylene from petroleum for gasoline blend stocks unlike in U.S.A. and the demands for solvents are also small. Moreover, their dealkylations to benzene may have little merit in Japan.

Those circumstances described above, made various processes for terephthalic acid synthesis take part in the severe commercial race, as shown in Table 1.

Table 1 shows that the process starting from *p*-xylene affords the largest portion of the total capacity and is expected to occupy 70% about the end of 1967. Those facts suggest that the *p*-xylene route is the most reasonable among several ways of supplying

terephthalic acid to polyester fibre makers, so the process may be applied to the additional terephthalic acid plants in Japan.

6. Miscellaneous

The selective extraction of *m*-xylene from mixed xylene has been successfully tested with a pilot plant by Japan Gas Chem. Ind. Co. The raffinate may be easily fractionated into *p*-xylene, *o*-xylene and ethylbenzene, it is claimed.

Sekisui Chem. Co. have tested the synthesis of ethylbenzene by cracking-alkylation from the light fraction of cracked gasoline byproduced at an ethylene-producing plant.

Ube Kosan Co. have developed their own process for synthesizing terephthalic acid from pot. benzoate, carbon monoxide and pot. carbonate.

Fuji Iron & Steel Co., Ube Kosan Co. and Kanto Electrochemical Co. have commercially practised the catalytic hydrogenation of benzene to cyclohexane by their own processes respectively.

Literatures

- 1) Amemiya, T., Hayashi, K., "The 6th World Petr. Congress", Sect. IV, No. 25.
- 2) Nakamura, E. et al., *J. Petrol. Inst.*, **9**, 634 (1966).
- 3) Ito, Y., *Bull. Chem. Soc. Japan*, **29**, 227 (1956).
- 4) Japanese Pat. No. 216,535 (1953).
- 5) Aikawa, K., *Hydrocarbon Processing*, **43**, (11), 157 (1964).
- 6) Ito, Y., *Chemistry & Industry (Japan)*, **18**, 1066 (1965).
- 7) Amemiya, T. et al., *J. Petrol. Inst.*, **3**, 813, 988 (1960); **4**, 201, 205, 210, 683 (1961).
- 8) Japanese Pat. No. 254,185 (1959); No. 254,186 (1959); No. 262,648 (1960); No. 270,166 (1961); No. 304,186 (1963); No. 307,343 (1963).