Kirk-Othmer Encyclopedia of Chemical Technology.

XYLENES AND ETHYLBENZENE

Xylenes and ethylbenzene [100-41-4] (**EB**) are C_8 aromatic isomers having the molecular formula C_8H_{10}. The xylenes consist of three isomers; *o*-xylene [95-47-6] (**OX**), *m*-xylene [108-38-3] (**MX**), and *p*-xylene [106-42-3] (**PX**). These differ in the positions of the two methyl groups on the benzene ring. The molecular structures are shown below.

1. Sources and Uses

The term *mixed xylenes* describes a mixture containing the three xylene isomers and usually EB. Commercial sources of mixed xylenes include catalytic reformate, pyrolysis gasoline, toluene disproportionation product, and coke-oven light oil. Ethylbenzene is present in all of these sources except toluene disproportionation product. Catalytic reformate is the product obtained from catalytic reforming processes. In catalytic reforming, a low octane naphtha cut (typically a straight run or hydrocracked naphtha) is converted into high octane aromatics, including, benzene, toluene, and mixed xylenes (see BTX processing). Aromatics are separated from the reformate using a solvent such as diethylene glycol or sulfolane and then stripped from the solvent. Distillation is then used to separate the BTX into its components. The amount of xylenes contained in the catalytic reformate depends on the fraction and type of crude oil, the reformer operating conditions, and the catalyst used. The amount of xylenes produced can vary widely, typically ranging from 18 to 33 vol % of the reformate. In the United States, only about 12% of the xylenes produced via catalytic reforming is actually recovered for use as petrochemicals. The unrecovered reformate xylenes are used in the gasoline pool.

Pyrolysis gasoline is a by-product of the steam cracking of hydrocarbon feeds in ethylene crackers (see Ethylene). Pyrolysis gasoline typically contains about 50–70 wt % aromatics, of which roughly 50% is benzene, 30% is toluene, and 20% is mixed xylenes (which includes EB).

Coke oven light oil is a by-product of the manufacture of coke for the steel industry. When coal is subjected to high temperature carbonization, it yields 16–25 liters/tonne of light oil that contains 3–6 vol % of mixed xylenes.

Toluene disproportionation (TDP) is a catalytic process in which 2 moles of toluene are converted to 1 mole of xylene and 1 mole of benzene; this process is discussed in greater detail herein. Although the mixed xylenes from TDP are generally more costly to produce than those from catalytic reformate or pyrolysis gasoline, their principal advantage is that they are very pure and contain essentially no EB.

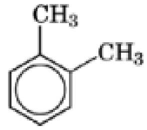
A breakdown of the mixed xylene supply sources in the United States is summarized in Table 1 (1). As shown in Table 1, the primary source of xylenes in the United States is catalytic reformate. In 1992, over 90% of the isolated xylenes in the United States were derived from this source. Approximately 9% of the recovered xylenes is produced via toluene disproportionation (TDP). In the United States, only negligible amounts of the xylenes are recovered from pyrolysis gasoline and coke oven light oil. In other parts of the world, pyrolysis gasoline is a more important source of xylenes.

Table 1. U.S. Supply Source for Mixed Xylenes[a]

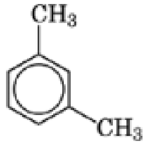
	Xylenes, 10^3 t	
Sources	Contained	Recovered
catalytic reformate	31,603	3,766
pyrolysis gasoline	395	16
toluene disproportionation	362	362
coke oven light oil	3	3
Total	*32,363*	*4,147*

[a] Ref. 1.

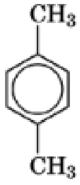
The mixed xylenes that are recovered from these sources are used as follows: 50–60% to make PX, 10–15% to make OX, 10–25% returned back to gasoline blending, and only 1% to make MX. The relative lack of end uses for MX is unfortunate, because these supply sources typically contain twice as much MX as PX or OX. The majority of the MX in these sources is isomerized to PX and OX, as discussed herein. The purified xylenes are used to synthesize plasticizers and polyester fibers, photographic films, and beverage bottles. PX is first oxidized to terephthalic acid or dimethyl terephthalate before being converted into polyesters. OX is oxidized to phthalic anhydride before being converted into plasticizers. MX is oxidized to isophthalic acid, which is used to make polyesters.



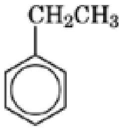
o-Xylene (OX)



m-Xylene (MX)



p-Xylene (PX)



Ethylbenzene (EB)

2. Physical Properties

Because of their similar molecular structures, the three xylenes and EB exhibit many similar properties (see Table 2). The very close boiling points of these compounds makes it difficult to separate them from each other by conventional distillation. OX is the easiest to distill from a mixture because of the 5°C difference in boiling point between it and the next closest boiling isomer, MX. This distillation is practiced commercially using one or two columns having a total of about 150 trays and a high reflux ratio. EB can also be separated from the mixture by distillation. However, this superfractionation requires several columns having a total of more than 300 theoretical trays. This method is highly energy-intensive compared to the production of EB via alkylation of benzene with ethylene. In the United States, Philbro Energy has operated a superfractionating facility, but this unit is currently shut down. Virtually no EB is currently made in the United States by superfractionation.

PX is not separated via distillation because its boiling point is too close to that of MX. Instead, the differences in freezing points and adsorption characteristics are exploited commercially, as described in detail herein.

Since xylenes are important components of gasoline, their combustion and octane characteristics are of interest. The critical compression ratios are 14.2, 1.36, and 9.6 for PX, MX, and OX, respectively. The research octane numbers are 116.4, 117.5, 107.4, and 113 for PX, MX, OX, and EB, respectively (7). The motor octane numbers are 110.0, 111.5, 100, and 105 for PX, MX, OX, and EB respectively.

3. Chemical Properties

Chemical reactions that the xylenes participate in include (*1*) migration of the methyl groups, (*2*) reaction of the methyl groups, (*3*) reaction of the aromatic ring, and (*4*) complex formation.

3.1. Migration of the Methyl Groups

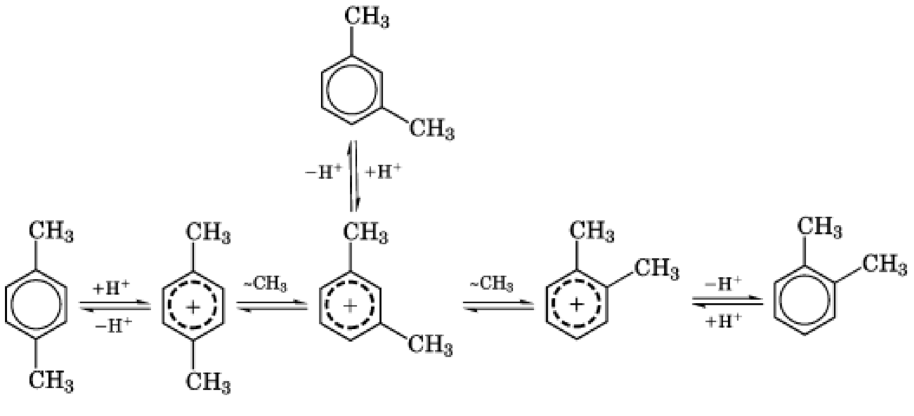
Reactions that involve migration of the methyl groups include isomerization, disproportionation, and dealkylation. The interconversion of the three xylene isomers via isomerization is catalyzed by acids. The acids can be liquids or solids. One example of an acidic liquid-phase system is hydrogen flouride–boron trifluoride (8). At low boron trifluoride concentrations, the xylenes isomerize to near equilibrium levels. At high boron trifluoride concentrations, a complex containing MX–hydrogen fluoride–boron trifluoride is formed which can be decomposed to produce high purity MX. Two other acidic liquid-phase systems that can isomerize the xylenes are hydrogen bromide in toluene and aluminum bromide in toluene (9). Examples of solid acids include aluminum-based materials and zeolites.

The mechanism of these reactions involves the rapid and reversible addition of a proton to the aromatic ring, followed by 1,2-intramolecular methyl shifts (10):

Table 2. Physical Properties for C_8 Aromatic Compounds[a]

Property	*p*-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene
molecular weight	106.167	106.167	106.167	106.167
density at 25°C, g/cm^3	0.8610	0.8642	0.8802	0.8671
boiling point, °C	138.37	139.12	144.41	136.19
freezing point, °C	13.263	−47.872	−25.182	−94.975
refractive index at 25°C	1.4958	1.4971	1.5054	1.4959
surface tension[b], mN/m(= dyn/cm)	28.27	31.23	32.5	31.50
dielectric constant at 25°C	2.27	2.367	2.568	2.412
dipole moment of liquid[c] C·m	0	0.30	0.51	0.36
critical properties[b]				
critical density, mmol/cm^3	2.64	2.66	2.71	2.67
critical volume, cm^3/mol	379.0	376.0	369.0	374.0
critical pressure, MPa[d]	3.511	3.535	3.730	3.701
critical temperature, °C	343.05	343.90	357.15	343.05
thermodynamic properties[e]				
C_s at 25°C, J/(mol·K)[f]	181.66	183.44	188.07	185.96
S_s at 25°C, J/(mol·K)[f]	247.36	253.25	246.61	255.19
H_o–H_o at 25°C, J/mol[f]	44.641	40.616	42.382	40.219
$-(G_s - H_o/T)$ at 25°C, J/(mol·K)[f]	97.633	117.03	104.46	120.29
heats of transition, J/(mol·K)[f]				
vaporization at 25°C	42.036	42.036	43.413	42.226
formation at 25°C	−24.43	−25.418	−24.439	−12.456
vapor pressure, Antoine equation[g]				
A	6.1155	6.1349	6.1239	6.0821
B	1453.430	1462.266	1474.679	1424.255
C	215.307	215.105	213.686	213.206

[a] Convenient graphic representation of the change in property with temperature are given in Refs. 2 and 3.
[b] Ref. 4.
[c] To convert C·m to D, divide by 3.336×10^{-30}.
[d] To convert MPa to psi, multiply by 145.
[e] Refs. 5 and 6.
[f] To convert J to cal, divide by 4.184.
[g] $\log P_{kPa} = A - B/(C + t)$; ($\log P_{mmHg} = \log P_{kPa} + \log 7.50$).



As shown in Figure 1, the equilibrium concentration is affected slightly by temperature (11). The actual concentration is affected by the reaction rate and the initial concentration of each isomer. Deviations beyond

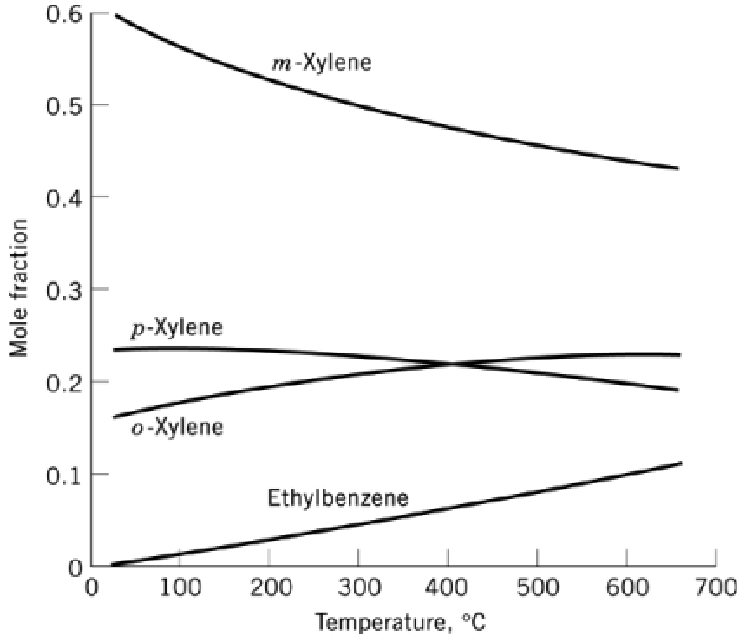


Fig. 1. Equilibrium concentrations for C_8 aromatic compounds (11).

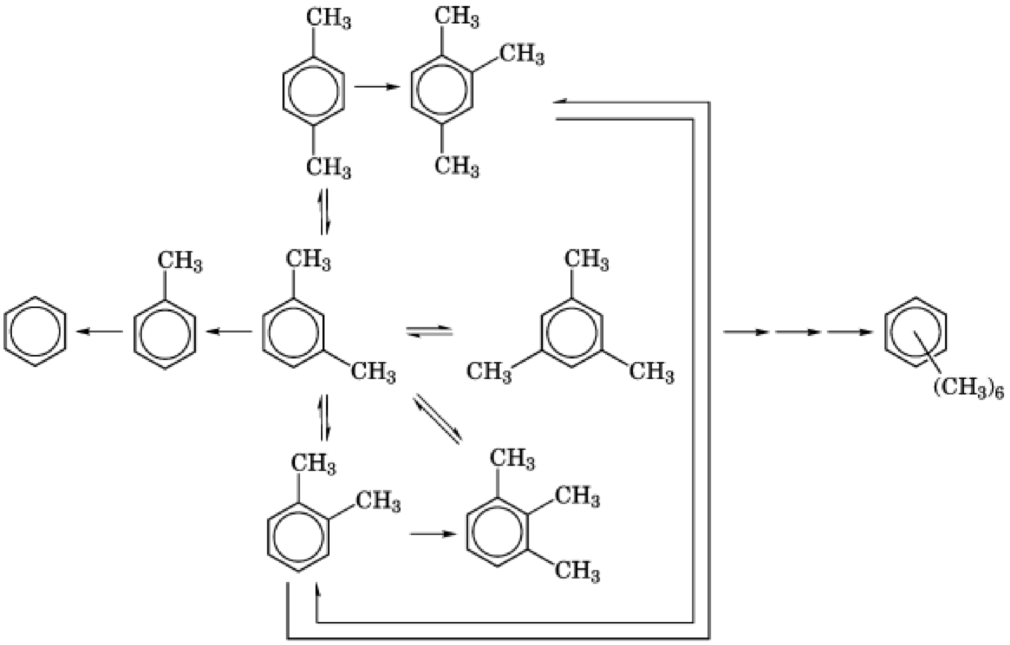
equilibrium can be achieved when zeolites are used, owing to shape selectivity (see Molecular sieves). The thermal isomerization of the three xylenes has been studied at 1000°C (12). Side reactions predominated, and only a small percentage of xylenes was interconverted.

Transalkylation is also catalyzed by acids, but requires more severe conditions than isomerization. As shown below, the methyl migration is intermolecular and ultimately produces a mixture of aromatic compounds ranging from benzene to hexamethylbenzene. The overall equilibrium constants for all possible methylbenzenes have been determined experimentally and calculated theoretically (Fig. 2 and Table 3).

Table 3. Overall Equilibrium Constants of Methylbenzenes[a]

	K_{eq}[b,c]			
Hydrocarbon	Reference 15	Reference 16	Reference 17	HCJ[d] and inductive model[a]
benzene		0.09	2×10^{-4}	$1 - 2 \times 10^{-4}$
toluene	~0.01	0.63	0.25	0.11–0.13
OX	2	1.1		1.8
MX	20	26	300	90–110
PX	1	1	1	1
pseudocumene	40	63		110–140
hemimellitene	40	69		200–310
durene	120	140		510–810
prehnitene	170	400		960–1700
mesitylene	2800	1.3×10^4	2×10^5	$2 - 3.6 \times 10^4$
isodurene	5600	1.6×10^4		$0.6 - 1 \times 10^5$
pentamethylbenzene	8700	2.9×10^4		$1.1 - 2.5 \times 10^5$
hexamethylbenzene	8.0×10^4	9.7×10^4	1×10^7	$0.7 - 1.5 \times 10^6$

[a] Ref. 14.
[b] Compared to PX.
[c] Column headings indicate sources of various test results.
[d] HCJ = hyperconjugative.



3.2. Reactions of the Methyl Groups

These reactions include oxidation, polycondensation, and ammoxidation. PX can be oxidized to both terephthalic acid and dimethyl terephthalate, which are then condensed with ethylene glycol to form polyesters. Oxidation of OX yields phthalic anhydride, which is used in the production of esters. These are used as plasticizers for

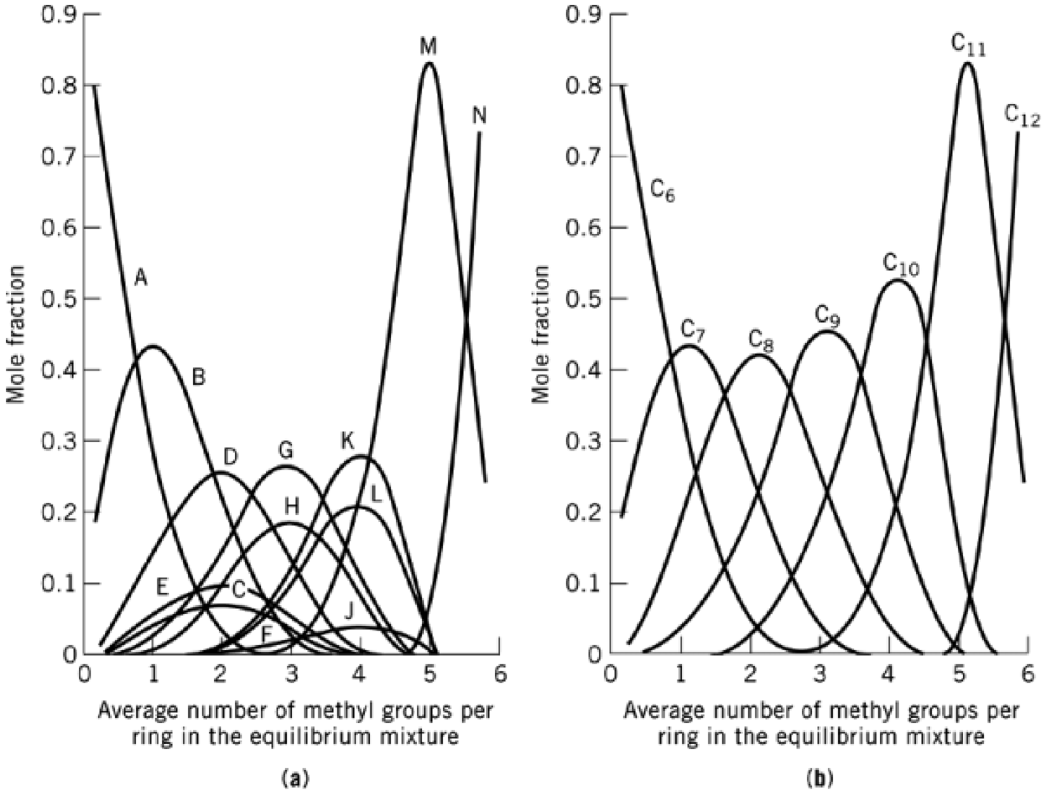
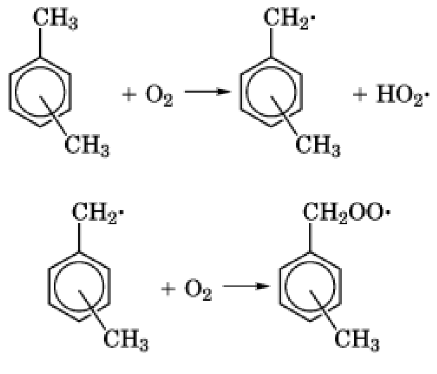


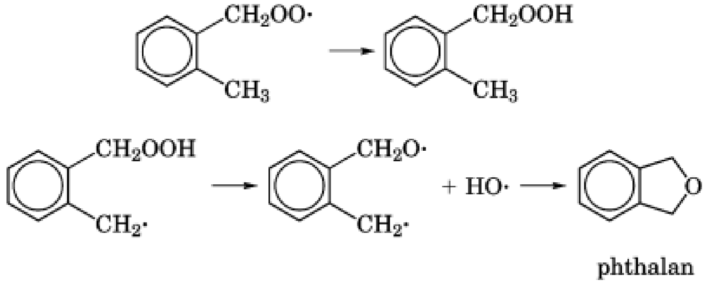
Fig. 2. Equilibrium concentrations of methyl benzenes in ideal gas state at 25°C (13). A=benzene; B=toluene; C=OX; D=MX; E=PX; F=hemimellitene; G=pseudocumene; H=mesitylene; J=prehnitene; K=isodurene; L=durene; M=pentamethylbenzene; N=hexamethylbenzene.

synthetic polymers. MX is oxidized to isophthalic acid, which is also converted to esters and eventually used in plasticizers and resins (see Phthalic acids and other benzenepolycarboxylic acids).

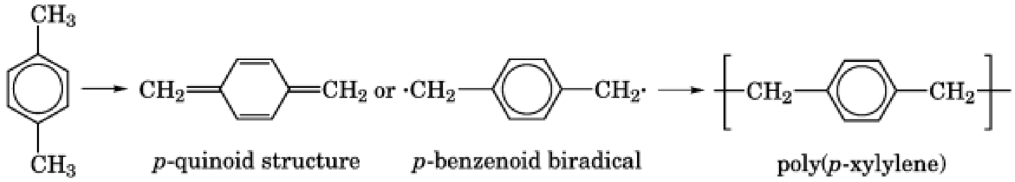
In a study of the slow combustion of the three xylenes, it was observed that OX is much more reactive toward oxygen than MX and PX (18). Under identical conditions, OX was approximately ten times as reactive as its isomers. It was proposed that the initial steps in the mechanisms of formation of each isomer are the same.



In the oxidation of PX and MX, formaldehyde is a degenerate branching intermediate, whereas phthalan is formed from OX:



PX forms p-xylylene when heated above 1200°C. The structure of p-xylylene is represented by a p-quinoid structure or as a p-benzenoid biradical. Condensation yields poly(p-xylylene) (19–22) (see Xylene polymers).



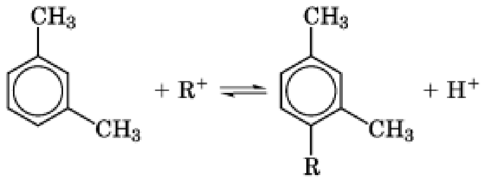
The methyl groups on xylenes can undergo ammoxidation, reaction with ammonia and oxygen (23).

$$2\ RCH_3 + 2\ NH_3 + 3\ O_2 \longrightarrow 2\ RCN + 6\ H_2O$$

The Showa Denka Company practices this reaction with a PX–MX mixture (24), whereas Mitsubishi Gas Chemical Company uses high purity MX first to form the dicyanide (25). In both processes, hydrogenation to the diamine follows. m-Xylenediamine is reacted with phosgene to give m-xylene diisocyanate, which is used in urethane resins (26–28).

3.3. Reactions of the Aromatic Ring

The reactions of the aromatic ring of the C_8 aromatic isomers are generally electrophilic substitution reactions. All of the classical electrophilic substitution reactions are possible (see Friedel-crafts reactions), but in most instances they are of little practical significance. The relative nuclear chlorination rates of polymethylbenzenes have been studied (29, 30). The higher the degree of substitution, the higher is the rate of chlorination.



As in most electrophilic reactions, the ability to stabilize the positive charge generated by the initial addition strongly affects the relative rates. MX reacts faster than OX and PX because both methyl groups work in conjunction to stabilize the charge on the next-but-one carbon. Sulfonation was, at one time, used to separate MX from the other C_8 aromatic isomers. MX reacts most rapidly to form the sulfonic acid which remains in the aqueous phase. The sulfonation reaction is reversible, and MX can be regenerated.

Hydrogenation of the aromatic ring to form naphthenic compounds has been proposed as a route to facilitate the separation of the C_8 aromatic isomers (31). The spread in boiling points of the naphthenic compounds is 12°C vs a spread of 8°C for the aromatic compounds. However, the cycloparaffinic products obtained from OX and EB boil only 3°C apart, impeding the separation.

3.4. Complex Formation

All four C_8 aromatic isomers have a strong tendency to form several different types of complexes. Complexes with electrophilic agents are utilized in xylene separation. The formation of the $HF–BF_3–MX$ complex is the basis of the Mitsubishi Gas–Chemical Company (MGCC) commercial process for MX recovery, discussed herein. Equimolar complexes of MX and HBr (mp $-77^\circ C$) and EB and HBr (mp $-103^\circ C$) have been reported (32, 33). Similarly, HCl complexes undergo rapid formation and decomposition at $-80^\circ C$ (34).

Werner complexes can be used to form clathrates with the C_8 aromatic isomers (35–42). The aromatic compounds are released upon heating. Since the uptake and release characteristics of the four C_8 aromatic isomers are each different, this method has been suggested as a means of separating the isomers.

Inclusion compounds of the C_8 aromatic compounds with tris(*o*-phenylenedioxy)cyclotriphosphazene have been used to separate the individual isomers (43–47). The Schardinger dextrins, such as alpha-cyclodextrin, beta-dextrin, and gamma-dextrin are used for clathration; alpha-dextrin is particularly useful for recovering PX from a C_8 aromatic mixture (48, 49). Pyromellitic dianhydride (50) and beryllium oxybenzoate (51) also form complexes, and procedures for separations were developed.

A 1:1 complex melting at 24.8°C is formed between PX and carbon tetrachloride (52). The other C_8 aromatic compounds do not form these complexes. Carbon tetrabromide and chloral (CCl_3CHO) form addition compounds with PX.

4. Manufacture of Xylenes

The initial manufacture of mixed xylenes and the subsequent production of high purity PX and OX consists of a series of stages in which (*1*) the mixed xylenes are initially produced; (*2*) PX and/or OX are separated from the mixed xylenes stream; and (*3*) the PX- (and perhaps OX-) depleted xylene stream is isomerized back to an equilibrium mixture of xylenes and then recycled back to the separation step. These steps are discussed below.

4.1. Mixed Xylenes Production Via Reforming

Again, two principal methods for producing xylenes are catalytic reforming and toluene disproportionation. A general schematic for the production of PX and OX (along with benzene and toluene) via catalytic reforming is shown in Figure 3 (see BTX processing). In this example, a light fraction (ie, 65–175°C) from a straight run petroleum fraction or from an isocracker is fed to a catalytic reformer, unit A. This is followed by heart-cutting and extraction in units B, C, and D. The mixed xylenes stream must then be processed further to produce high purity PX and/or OX. As discussed herein, high purity OX can be produced via distillation. However, because of the close boiling points of PX and MX, using distillation to produce high purity PX is impractical. Instead, other separation methods such as crystallization and adsorption are used. These separation processes are discussed herein.

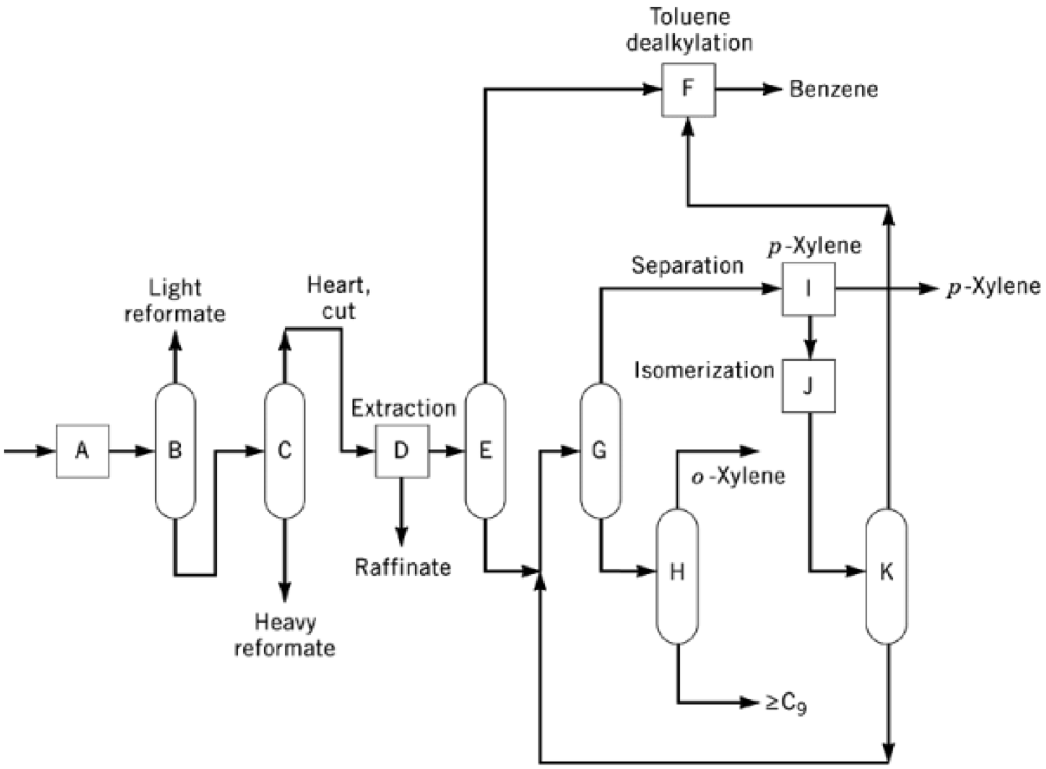
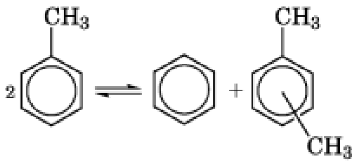


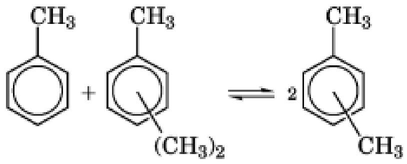
Fig. 3. General scheme for producing benzene, PX, and OX from catalytic reforming.

4.2. Xylenes Production Via Toluene Transalkylation and Disproportionation

The toluene that is produced from processes such as catalytic reforming can be converted into xylenes via **transalkylation** and **disproportionation**. Toluene disproportionation is defined as the reaction of 2 mol of toluene to produce 1 mol of xylene and 1 mol of benzene. Toluene transalkylation is defined as the reaction of toluene with C_9 or higher aromatics to produce xylenes:



Disproportionation



Transalkylation

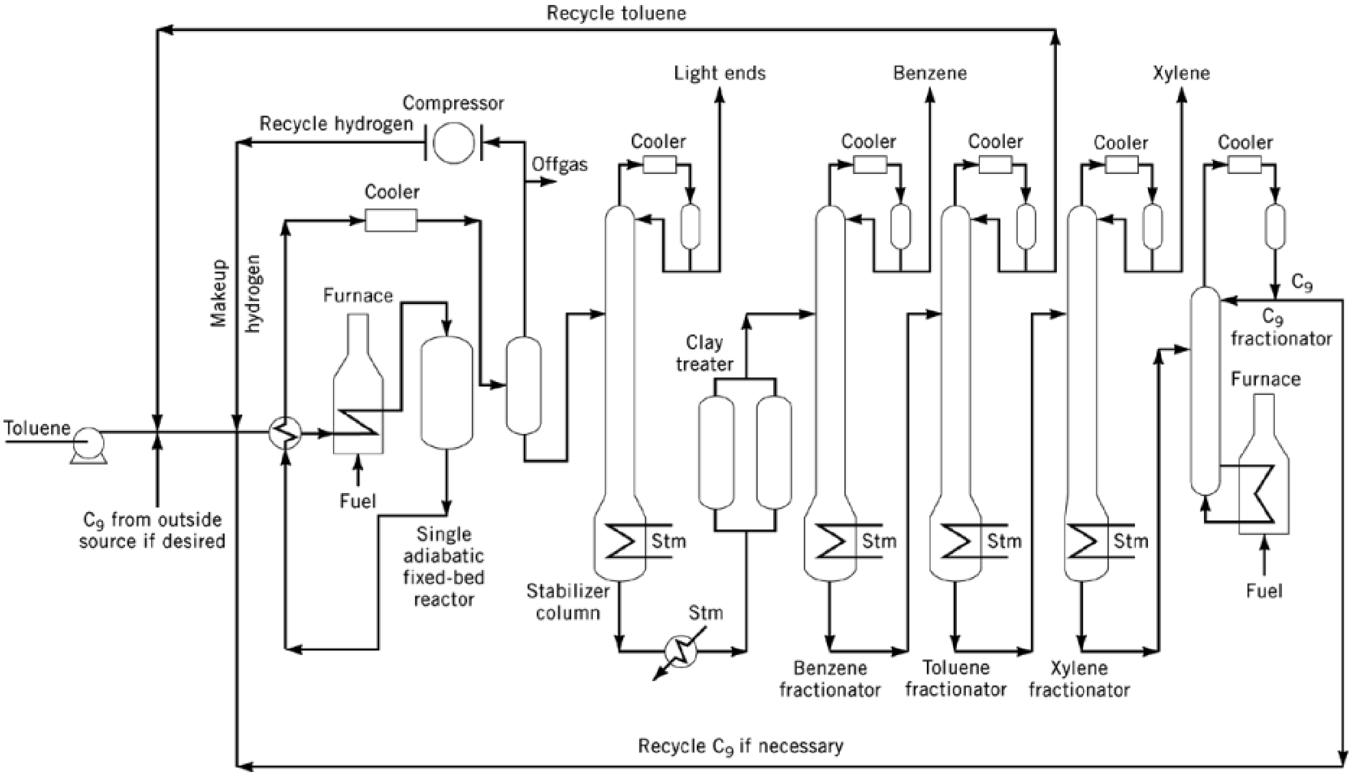


Fig. 4. UOP Tatoray process for xylenes production.

Table 4. Tatoray Transalkylation of Toluenes and C_9 Aromatic Compounds, Relative Wt Units

Feed		Product		
Toluene	C_9 Aromatics	Xylenes	Benzene	Other
1000	0	460	425	125
500	500	675	200	125

Other species that are also present in the feed, such as ethylbenzene and methylethylbenzenes will also undergo transalkylation reactions. These reactions tend to approach an equilibrium that depends on the operating conditions.

There are several commercial processes that produce xylenes via disproportionation or transalkylation. These include UOP's Tatoray and PX-Plus, ARCO's Xylenes Plus, and Mobil's MTDP and STDP.

The Tatoray process was originally developed by Toray and is currently licensed by UOP (53–57). A schematic of the process is shown in Figure 4. In this process, toluene or a mixture of toluene and C_{9+} aromatics are reacted to form primarily xylenes and benzene. An equilibrium distribution of xylenes is produced. As shown in Table 4, the ratio of xylenes to benzene can be adjusted by altering the feed ratio to toluene to C_9 aromatics. Trimethylbenzenes are the preferred C_9 aromatic compound.

Table 5. Xylenes Plus Transalkylation of Toluene and C_9 Aromatics Compounds, Relative Wt Units

Feed		Product		
Toluene	C_9 Aromatic Compounds	Xylenes	Benzene	Other
1000	0	460	430	120
500	500	700	140	120

Catalyst improvements have been made since the process was first developed. The current catalyst is designated TA-4 (57). It has a high per pass conversion and good stability. Yields to xylenes are reported to be over 97%. The pelleted catalyst is used in a fixed-bed reactor in the presence of hydrogen. Typical operating conditions are: 350–530°C, 1–5 MPa (10–50 atm), and H_2/ hydrocarbon ratio of 5–12:1. Toluene per pass conversion is about 40–50%. Per pass conversion can be increased by increasing pressure or temperature, although this also reduces yield and increases the rate of catalyst deactivation. The product typically contains <2 mol% EB. The catalyst is regenerated by burning of the coke that is formed. The first commercial plant was built at Toray's Kawasaki plant in 1969. As of 1995, 32 units are reported to have been licensed (57).

The Xylenes Plus process also converts toluene with or without C_{9+} aromatics. This process was originally developed by ARCO and is also currently available for license from Lyondell and HRI/IFP (58, 59). Feeds that have been commercially used include catalytic reformate and hydrotreated pygas. The catalyst is reported to be a nonnoble metal catalyst. A moving bed system is used with a continuous catalyst regenerator. Hydrogen is not required for any facet (start-up, operation, or catalyst regeneration) of the process, and thus operating pressure is relatively low. The licensors report that operation at 30% toluene per pass conversion results in the highest possible yield of xylenes with minimal feedstock loss to gas or coke. EB production is close to zero. Liquid yields are reported to be 95–97 vol % with an equilibrium distribution of xylenes ($PX/OX/MX = 26/24/50$). The yields of xylenes and benzene for various feed ratios of toluene and C_9 aromatics are given in Table 5. The first plant was installed at ARCO's (now Lyondell's) Houston refinery in 1968. To date, this process has been utilized at 5 plants worldwide.

Mobil has developed several TDP processes. In the 1970s, Mobil developed their LTD (Low Temperature Disproportionation) process (60, 61). This was a liquid-phase process which used what was described as siliceous zeolitic catalysts. Hydrogen was not required in the process. Reactor pressure was 4.5 MPa and WHSV of 0.68 kg oil/h kg catalyst. The initial reactor temperature was 127°C and was raised as the catalyst deactivated to maintain toluene conversion. The catalyst was regenerated after the temperature reached about 315°C. Regeneration consisted of conventional controlled burning of the coke deposit. The catalyst life was reported to be at least 1.5 yr.

In the mid-1970s, Mobil introduced their MTDP process (62). This is a vapor-phase process that uses ZSM-5-type zeolites. The process operates at 48 wt % toluene per pass conversion with a near equilibrium PX selectivity of 24% in the xylenes product. Typical operating conditions are inlet temperatures of 390–495°C, H_2 partial pressure of 4.1 MPa, H_2/hydrocarbon molar ratio of 4, and liquid hourly space velocity $(LHSV) = 1.0 - 2.0/h$. EB production was about 3 wt % of feed. The first commercial use of this process was at Mobil's Naples, Italy petrochemical complex in 1975. In the 1980s, Mobil developed an improved ZSM-5 catalyst formulation for the MTDP process which was reported to have significant activity and stability advantages over the first catalyst. The higher activity of the improved catalyst meant reactor temperatures could be lowered by about 55°C, resulting in lower coking rates and longer catalyst cycle times. Hydrogen partial pressures could also be lowered. The latest version of MTDP is designated MTDP-3 (63). To date six commercial units have been installed using MTDP technology.

In the late 1980s, Mobil commercialized the MSTDP (Mobil Selective Toluene Disproportionation) Process (64–66). In MSTDP, PX selectivity can be boosted to 80–90% at toluene conversion of about 25–30%. The significantly higher than equilibrium yield of PX is obtained by precoking the catalyst in the reactor. This reduces the pore size opening of the ZSM-5 catalyst and also meliminates acidity on the external surface which can cause reisomerization back to equilibrium. Inside the catalyst pores, an equilibrium mix of the three xylene isomers is obtained. However, the smaller molecular dimensions of PX compared to OX and MX translates into a relative diffusivity for PX that is several orders of magnitude higher than that of OX and MX. Because of its higher diffusivity, PX exits the catalyst pores more rapidly while the remaining OX and MX reequilibrate inside the pores to form more PX. The catalyst is initially selectivated in the reactor by precoking with toluene. This pretreatment is performed at the beginning of each cycle. As coking occurs, the toluene conversion progressively drops from 60% to about 20–30%, whereas the PX selectivity increases from 24% to about 80–90%. The higher PX concentration produced in the MSTDP process compared to conventional TDP processes means that the subsequent crystallization or adsorption PX recovery facilities can be significantly smaller. Typical operating conditions are: 400–470°C, 2.0–3.4 MPa, $\text{WHSV} = 2-4/\text{h}$, H_2/hydrocarbon molar ratio of 1–3:1. The MSTDP process was first demonstrated at Enichem's refinery in Gela, Italy in 1988. As of mid-1996, 9 units had been licensed. Of these, six are currently operating, including a reformer retrofit by Exxon and a grass roots unit by Koch in the United States, while three others were scheduled for start-up before the end of 1997.

In 1995, Mobil announced an improved MSTDP process named MTPX (Mobil Toluene to Paraxylene) (67). Although there are no technical details of this process in the technical literature at the present time, at least some of the improvement may consist of doing the catalyst pore selectivation with the organosilicones that are the subject of a recent Mobil Patent (68). Unlike the coking selectivation, this treatment could be done during catalyst manufacture. Mobil has also announced that it does not plan to license this technology and no longer plans to offer new MSTDP licenses (69). Mobil has built a grassroots MTPX plant at its Beaumont plant.

In 1997, UOP announced the PX-Plus process which also uses a selectivated catalyst to convert toluene to para-rich xylenes. Fina commercialized a TDP process known as the (T2PX) process in 1984 (70). It uses a proprietary catalyst to react toluene at 42–48% conversion with selectivities to benzene of 42 wt % and to xylenes of 46 wt %. The xylenes produced are at equilibrium. Typical commercial operating conditions of 390–495°C, H_2 partial pressure of 4.1 Mpa, H_2/hydrocarbon molar ratio of 4:1, and LHSV of 1–2/h. Fina's first commercial implementation occurred in 1985 at their Port Arthur refinery.

4.3. Separation Processes for PX

There are essentially two methods that are currently used commercially to separate and produce high purity PX: (*1*) crystallization and (*2*) adsorption. A third method, a hybrid crystallization/adsorption process, has been successfully field-demonstrated and the first commercial unit is expected in the near future.

4.3.1. Crystallization

Low temperature fractional crystallization was the first and for many years the only commercial technique for separating PX from mixed xylenes. As shown in Table 2, PX has a much higher freezing point than the other xylene isomers. Thus, upon cooling, a pure solid phase of PX crystallizes first. Eventually, upon further cooling, a temperature is reached where solid crystals of another isomer also form. This is called the eutectic point. PX crystals usually form at about −4°C and the PX-MX eutectic is reached at about −68°C. In commercial practice, PX crystallization is carried out at a temperature just above the eutectic point. At all temperatures above the eutectic point, PX is still soluble in the remaining C_8 aromatics liquid solution, called mother liquor. This limits the efficiency of crystallization processes to a per pass PX recovery of about 60–65%.

The solid PX crystals are typically separated from the mother liquor by filtration or centrifugation. Good solid/liquid separation is important for obtaining high purity PX. One key to good separation is crystal size. The larger the crystal, the better the separation. Crystal size is affected by the degree of supersaturation and nucleation, which in turn is affected by a number of parameters, including temperature, agitation, and the presence of crystal growth sites.

PX crystals are typically produced in two or more stages of crystallization, separated by centrifuges. Commercial crystallizers use either direct contact or indirect refrigeration. The latter has the disadvantage that the walls of the cooled surface tend to foul, which reduces heat transfer. The first crystallizer stage is usually at the lowest temperature. The cake from this stage has a purity of about 80–90%. The impurity arises from the mother liquor which wets the crystal surface or is occluded in the crystal cake. The efficiency of the solid–liquid separation depends on the temperature and the loading of the centrifuges. As temperature falls, the viscosity and density of the mother liquor rise sharply. Thus, it becomes more difficult for the centrifuges to achieve effective separation.

In the second crystallizer stage, the crystals are usually reslurried with a higher purity PX stream from a later stage of purification. A second stage of centrifugation is sufficient in most cases to give PX purity $>99\%$.

Currently, about 40% of the PX produced worldwide uses crystallization technology. A number of crystallization processes have been commercialized over the years. The more common ones are those developed by Chevron, Krupp, Amoco, ARCO (Lyondell), and Phillips. Some of the features of these processes are discussed herein.

The Chevron process (71) is shown in Figure 5. It consists of two crystallizers in series operated at difficult pressures. Direct contact cooling is used. This is accomplished by injecting liquid CO_2 with the feed to the crystallizer. As the slurry rises, part of the CO_2 vaporizes, causing the temperature to drop below the saturation temperature, and crystallization occurs. Because cooling is gradual, the degree of supersaturation is low and thus crystal growth occurs on the existing crystals. This leads advantageously to the formation of relatively large crystals, rather than many small ones. The crystals and slurry move down from the crystallizer body. Most of the slurry is recycled, but some is withdrawn and sent to the second crystallizer, which is operated under vacuum. The operation of the second crystallizer is similar to the first, except that typically it is not necessary to inject additional CO_2. The crystals are separated from the mother liquor in two stages. The first stage uses screen bowl centrifuges, and the second uses pusher centrifuges. The Chevron process offers the advantage that large crystals are obtained in a relatively short residence time, which permits good solid–liquid separation in the centrifuges. Plants using this process have been licensed and built in the United States, Germany, Mexico, Japan, and in the United Kingdom.

The Krupp process for PX crystallization uses scraped chillers for crystallization (72). Rotary drum filters and centrifuges are used for phase separation. The first-stage solids are reslurried in a PX-rich filtrate from the final PX product centrifuge. Another feature is that the second-stage mother liquor is further chilled and centrifuged before being passed back to the first-stage feed. The resultant solids are added to the first-stage crystals.

The Amoco PX crystallization process (73, 74) is a two-stage process that operates with indirect cooling. A schematic of this process is shown in Figure 6. Ethylene is used as the coolant in the first stage and propane is used in the second stage. In the first-stage crystallizer, the temperature is brought down in stages to near the PX–MX eutectic. The first stage cake is melted and sent to a second-stage crystallizer, which is designed like the first, but uses propane refrigerant instead of ethylene. The crystallizers are fitted with scrapers mounted on a central shaft, which provides agitation and maintains a good heat-exchange surface. The residence time in each of the two crystallizers is about 3 h, in order to encourage crystal growth.

The ARCO process is similar to the Amoco process in that it is a two-stage crystallization process that uses external ethylene refrigerant in the first stage and propane in the second stage (75, 76). The first stage consists of two crystallizers which operate at -40 to -50°C and -55 to -70°C, respectively. The first-stage slurry flows to a continuous centrifuge where crystals of 85–90% purity are removed from the filtrate. The crystals are remelted and then sent to a single second-stage crystallizer operated at -20 to 0°C, depending on the feedstock and desired purity. The crystal slurry flows from the crystallizer to a second-stage continuous centrifuge. The crystals are washed with toluene in the centrifuge and melted. The liquid is then fed to a PX–toluene splitter where high purity PX is taken as a bottoms product. Eight plants have been built worldwide.

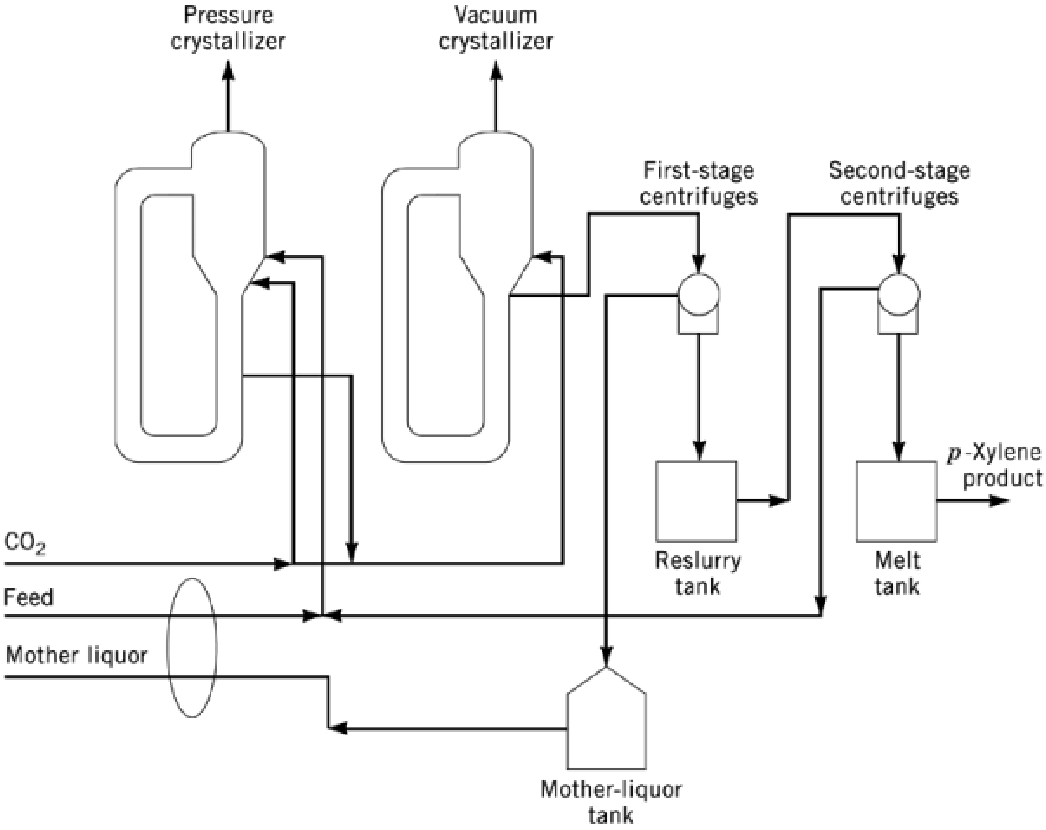


Fig. 5. Chevron PX crystallization process.

The Maruzen process uses ethylene gas as a direct refrigerant in a two-stage process (77, 78). The first stage slurry is centrifuged, partially remelted, and fed to the second centrifuge.

The Phillips process is a two-stage crystallization process that uses a pulsed column in the second stage to purify the crystals (79, 80). In the pulsed column, countercurrent contact of the high purity PX liquid with cold crystals results in displacement of impurities. In the first stage, a rotary filter is used. In both stages, scraped surface chillers are used. This process was commercialized in 1957, but no plants in operation as of 1996 use this technology.

Relatively recently, several companies have commercialized static crystallization processes based on progressive freezing. In progressive freezing, crystals are allowed to form on a cooled surface until a certain proportion of the original batch is frozen. The remaining melt is drained away from the solid layer. In some versions, the frozen layer is also gently warmed to sweat out impurities caught in the crystal structure. Finally, the PX is recovered by heating the surface to completely melt off the frozen layer. In systems developed by BEFS and Sulzer Chemtech, the crystal layer is grown on vertical cooled plates. In the BEFS PROKEM PROABD process, feed containing about 80–99.5% PX is further purified to 99.9+% in a single-stage melt static crystallizer (81). After crystallization, the crystalline mass is purified by a partial melting of the crystals to wash out adhering impurities. This process can be used as a finishing step to further improve the purity of PX product from adsorption, crystallization, or MSTDP units. An 8000-t/yr plant has been in operation for

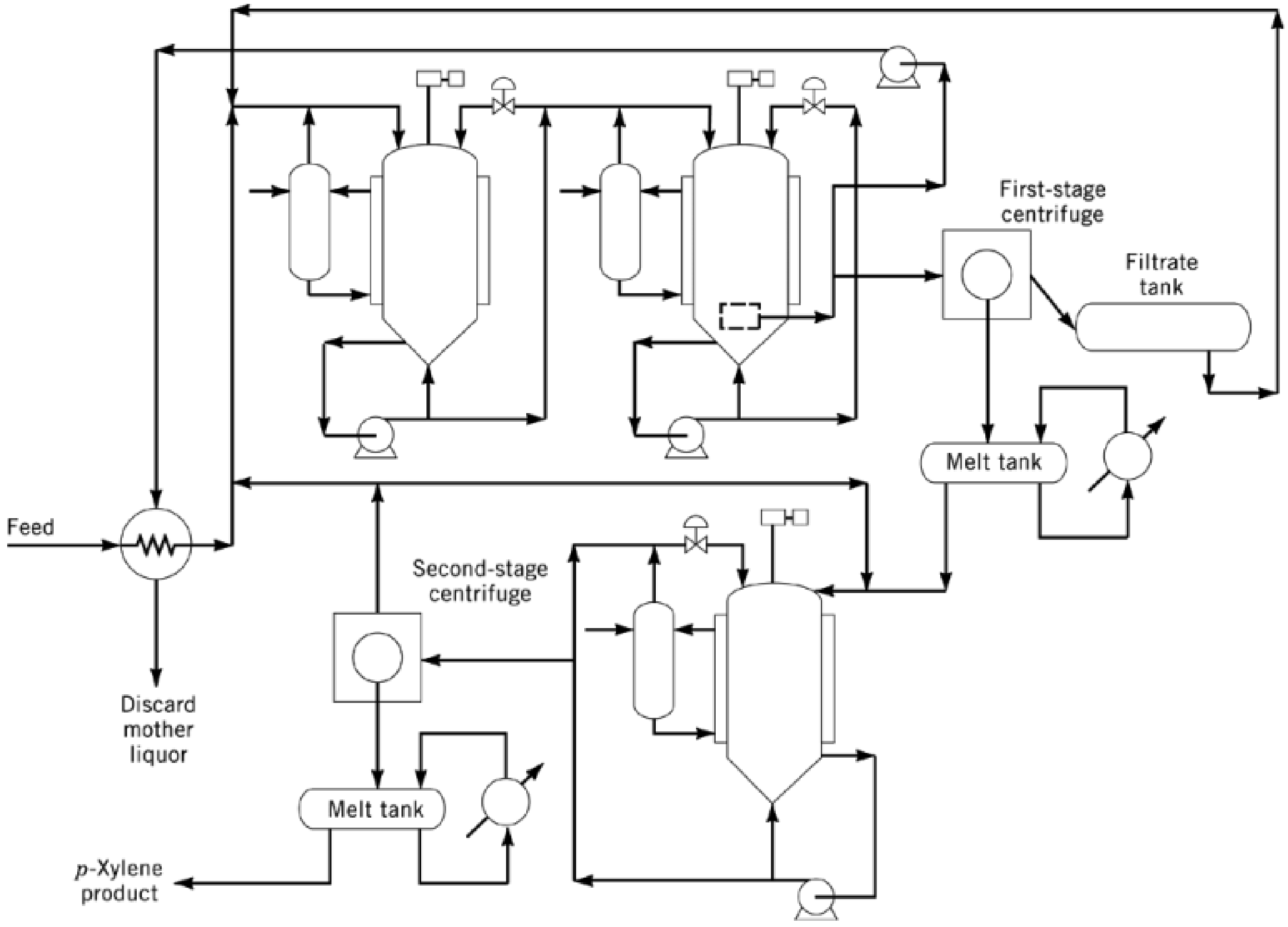


Fig. 6. Amoco PX crystallization process.

three years in Gonfreville, France. BEFS Prokem has recently won two contracts to implement the process at Reliance Industries in India and Neftochim E.A.D. in Bulgaria (82).

One drawback of static crystallization is that crystal layer growth rates are very slow. In the Sulzer MWB process, growth rates are greatly improved by allowing a film to flow down vertical tubes (83).

4.3.2. Adsorption Processes

Adsorption represents the second and newer method for separating and producing high purity PX. In this process, adsorbents such as molecular sieves are used to produce high purity PX by preferentially removing PX from mixed xylene streams. Separation is accomplished by exploiting the differences in affinity of the adsorbent for PX, relative to the other C_8 isomers. The adsorbed PX is subsequently removed from the adsorbent by displacement with a desorbent. Typical PX recovery per pass is over 95%, compared to only 60–65% for crystallization. Thus recycle rates to the separation and isomerization units are much smaller where adsorption is used.

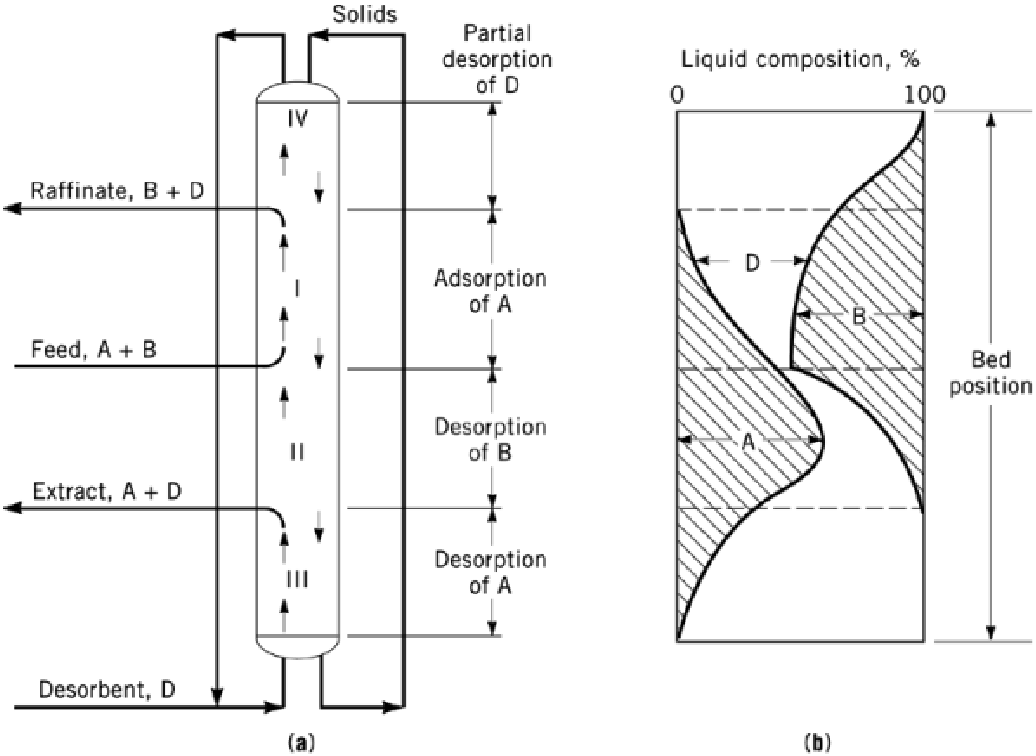


Fig. 7. Ideal PX adsorption process.(Courtesy of UOP.)

Currently, there are three commercially available PX adsorption processes: UOP's Parex, IFP's Eluxyl, and Toray's Aromax (not to be confused with Chevron's Aromax process for reforming naphtha into aromatics). In all of these processes, the feed and desorbent inlets and the product outlet ports are moved around the bed, simulating a moving bed.

In 1971, UOP first commercialized their PX adsorbent process, Parex (84–94). It is one of several adsorption processes that contitutes UOP's SORBEX adsorption technologies. Ideally, an adsorption process would be like the hypothetical moving-bed adsorption system in Figure 7**a**. In this system, solid adsorbent moves through the bed countercurrently to the liquid. The feed is assumed to be a binary mixture of component A (PX) and component B (MX, OX, and EB). Component A is selectively adsorbed. Desorbent D enters the top of the bed. Extract $(\mathrm{A} + \mathrm{desorbent})$ is withdrawn at a point between the desorbent and feed injection points. Raffinate containing $\mathrm{B} + \mathrm{desorbent}$ is withdrawn below the feed injection point. The adsorber is effectively divided into four separate zones. In zone 1, feed component A is completely adsorbed from the downward-moving liquid stream. Zone 2 is a rectification section where component B is completely desorbed from the adsorbent. Zone 3 is a desorbent section where A is displaced from the adsorbent by the desorbent D. Zone 4 is a secondary rectification section where component B is readsorbed, preventing B from entering zone 3 where it would contaminate the product A. The liquid composition in these four zones is illustrated in Figure 7**b**.

There are, however, several difficulties which prevent this ideal system from being literally implemented commercially. These include likely mechanical erosion of the adsorbent if it were to circulate in the bed and the difficulty of obtaining truly uniform flow of both solids and liquids in large-diameter beds. However, UOP recognized that the same results can be accomplished on a commercial scale by holding the bed stationary, but periodically moving the positions at which the various liquid streams enter and leave. By shifting the positions of feed-injection and product-withdrawal streams in the direction of flow through the bed, the countercurrent movement of solid is simulated. Although from a practical standpoint the fluid-injection and withdrawal positions cannot be moved continuously, nearly the same effect can be achieved by providing multiple liquid access lines to the bed and periodically switching each stream to the adjacent port, always maintaining the same relative distance between the various streams.

The flow diagram illustrating the commercial implementation of this fixed-bed continuous adsorption process by UOP is shown in Figure 8. The feed, desorbent, and product ports are continuously changed, using a patented rotary valve. In the particular example shown in Figure 8, 12 lines are connected to the rotary valve. Only four lines are active at any one instant. Desorbent is injected into one line, feed is injected into another, extract is withdrawn from another, and raffinate is withdrawn from still another. By rotating the valve by one position, a different set of four ports is activated. Thus a condition is simulated whereby the solid appears to be moving past fixed portions of fluid feed, product, and withdrawal. The operating conditions are 250–400°C and moderate pressures. Earlier versions of Parex used a light desorbent, toluene. More recent versions have used a heavier desorbent, usually *p*-diethylbenzene, which has resulted in lower energy costs associated with separating the PX from the desorbent. The newest adsorbent, ADS-27 was commercialized in 1990. Compared to its predecessor, ADS-7, UOP claims that capacity has increased 15%. Another reported benefit is that ADS-27 is manufactured and loaded into the commercial unit at the moisture level required for operation. This eliminates the need for the adsorbent to go through the initial vapor-phase benzene dry-down step required by previous adsorbents. The first Parex unit was commercialized in 1971. As of 1995, 59 units had been licensed (94).

The Aromax process was developed in the early 1970s by Toray Industries, Inc. in Japan (95–98). The adsorption column consists of a horizontal series of independent chambers containing fixed beds of adsorbent. Instead of a rotary valve, a sequence of specially designed on–off valves under computer control is used to move inlet and withdrawal ports around the bed. Adsorption is carried out in the liquid phase at 140°C, 785–980 kPA, and 5–13 L/h. PX yields per pass is reported to exceed 90% with a typical purity of 99.5%. The first Aromax unit was installed at Toray's Kawasaki plant in March 1973. In 1994, IFP introduced the Eluxyl adsorption process (59, 99). The proprietary adsorbent used is designated SPX 3000. Individual on–off valves controlled by a microprocessor are used. Raman spectroscopy to used to measure concentration profiles in the column. A 10,000 t/yr demonstration plant was started and successfully operated at Chevron's Pascagoula plant from 1995–96. IFP has licensed two hybrid units.

Asahi Chemical Industry Company Ltd. was working to develop an adsorption process in the late 1970s and early 1980s that was to produce high purity EB as well as PX (100–103). In 1981 they reported that pilot plants results were being confirmed in larger equipment. However, this process does not appear to have been commercialized.

4.3.3. Hybrid Crystallization/Adsorption Process

In 1994, IFP and Chevron announced the development of a hybrid process that reportedly combines the best features of adsorption and crystallization (59, 99). In this option of the Eluxyl process, the adsorbent bed is used to initially produce PX of 90–95% purity. The PX product from the adsorption section is then further purified in a small single-stage crystallizer and the filtrate is recycled back to the adsorption section. It is reported that ultrahigh (99.9+%) purity PX can be produced easily and economically with this scheme for both retrofits of existing crystallization units as well as grass-roots units. A demonstration plant was built at Chevron's Pascagoula refinery in 1994.

4.4. MX Separation Process

The Mitsubishi Gas–Chemical Company (MGCC) has commercialized a process for separating and producing high purity MX (104–113). In addition to producing MX, this process greatly simplifies the separation of the

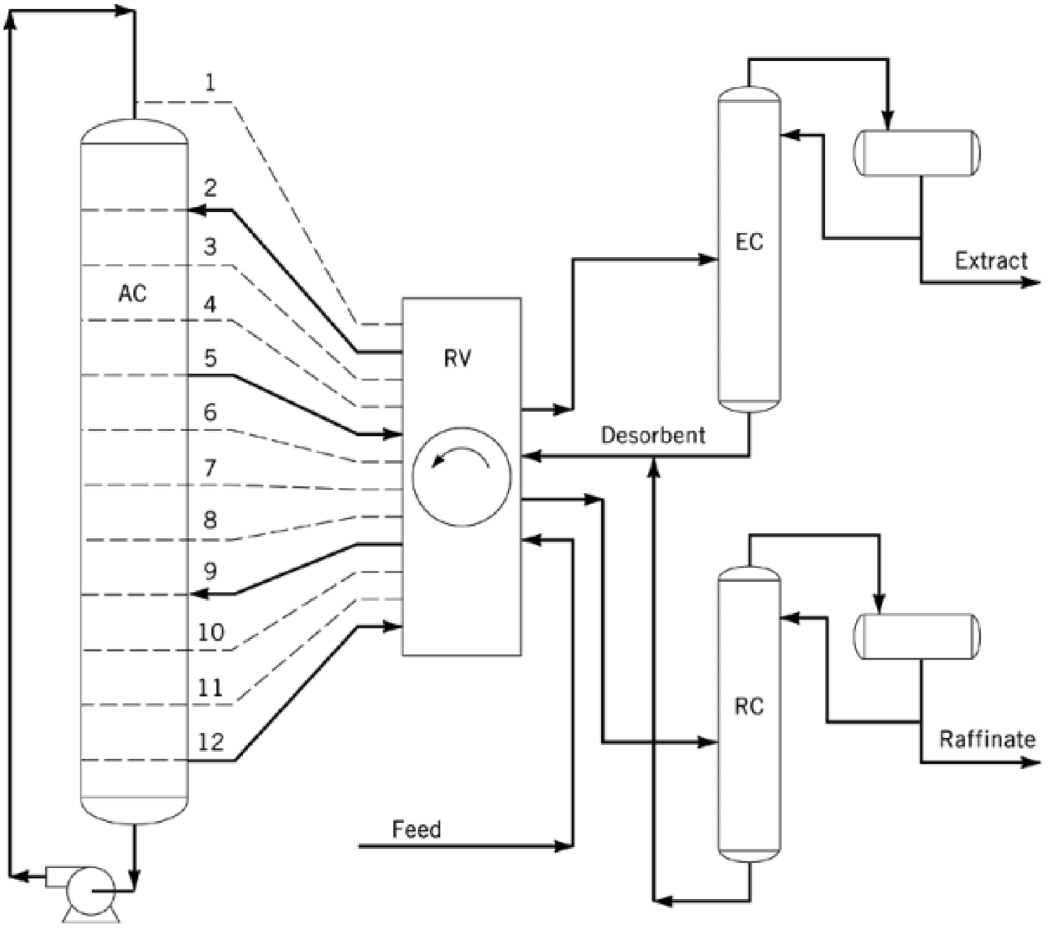


Fig. 8. UOP Parex simulated moving bed for adsorptive separation. AC=adsorbent chamber; RV=rotary valve; EC=extract column; RC=raffinate column. Lines: 2-desorbent; 5-extract; 9-feed; 12-raffinte. All other ports are closed at this time.

remaining C_8 aromatic isomers. This process is based on the formation of a complex between MX and HF–BF_3. MX is the most basic xylene and its complex with HF–BF_3 is the most stable. The relative basicities of MX, OX, PX, and EB are 100, 2, 1, and 0.14, respectively.

MX of $>99\%$ purity can be obtained with the MGCC process with $<1\%$ MX left in the raffinate by phase separation of hydrocarbon layer from the complex-HF layer. The latter undergoes thermal decomposition, which liberates the components of the complex.

A schematic of the MGCC process is shown in Figure 9. The mixed C_8 aromatic feed is sent to an extractor (unit A) where it is in contact with HF–BF_3 and hexane. The MX–HF–BF_3 complex is sent to the decomposer (unit B) or the isomerization section (unit D). In the decomposer, BF_3 is stripped and taken overhead from a condensor–separator (unit C), whereas HF in hexane is recycled from the bottom of C. Recovered MX is sent to column E for further purification. The remaining C_8 aromatic compounds and hexane are sent to raffinate column F where residual BF_3 and HF are separated, as well as hexane for recycle. Higher boiling materials are rejected in column H, and EB and OX are recovered in columns I and J. The overhead from J is fed to unit K for PX separation. The raffinate or mother liquor is then recycled for isomerization.

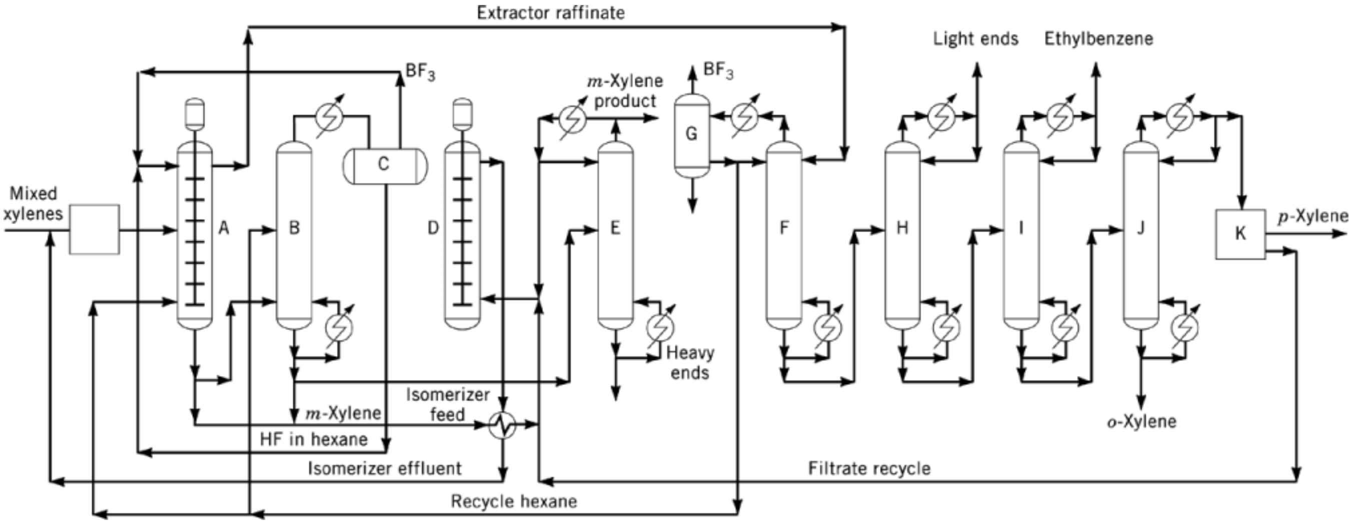


Fig. 9. Xylenes separation via Mitsubishi Gas–Chemical Co. HF-BF_3 extraction–isomerization process (107). A=extractor; B=decomposer; C=separator; D=isomerization reactor; E=heavy ends tower; F=raffinate tower; G=separator; H=light ends fractionator; I=ethylbenzene fractionator; J=OX fractionator; K=PX crystallizer.

The MGCC process is used in Japan, the United States, and Spain.

4.5. Xylene Isomerization

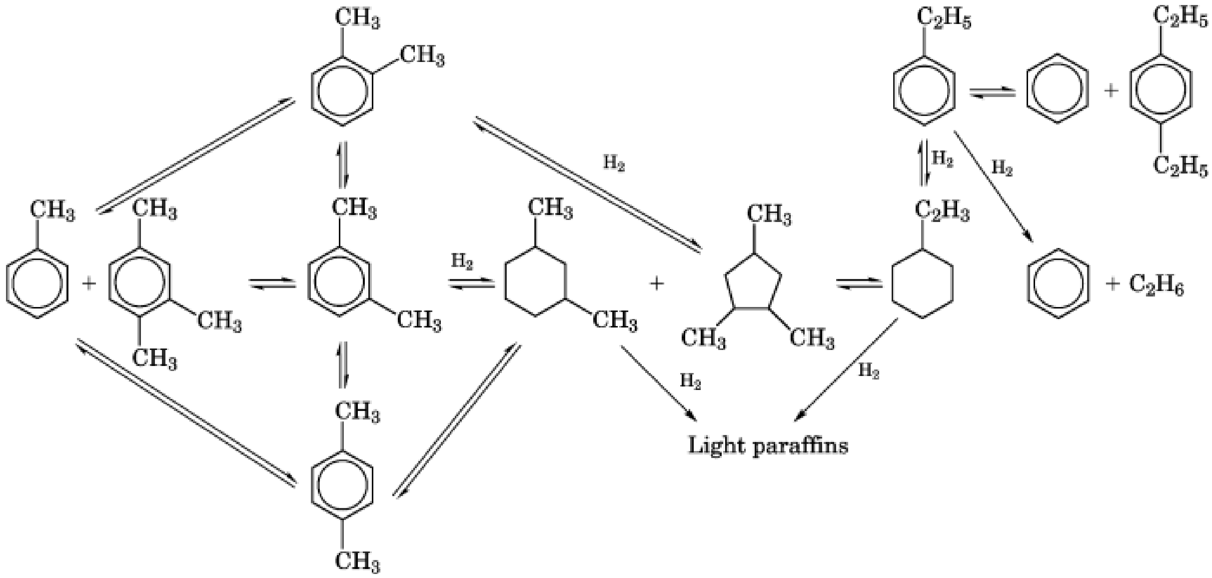
After separation of the preferred xylenes, ie, PX or OX, using the adsorption or crystallization processes discussed herein, the remaining raffinate stream, which tends to be rich in MX, is typically fed to a xylenes isomerization unit in order to further produce the preferred xylenes. Isomerization units are fixed-bed catalytic processes that are used to produce a close-to-equilibrium mixture of the xylenes. To prevent the buildup of EB in the recycle loop, the catalysts are also designed to convert EB to either xylenes, benzene and lights, or benzene and diethylbenzene.

Historically, the isomerization catalysts have included amorphous silica–aluminas, zeolites, and metal-loaded oxides. All of the catalysts contain acidity, which isomerizes the xylenes and if strong enough can also crack the EB and xylenes to benzene and toluene. Dual functional catalysts additionally contain a metal that is capable of converting EB to xylenes.

The three major commercial licensors of xylenes isomerization processes are Engelhard, UOP, and Mobil. Several other companies have developed and used their own catalysts. These companies include Mitsubishi Gas–Chemical, Toray, ICI, Amoco, and Shell. All of these processes are discussed herein.

4.5.1. Dual Function Catalytic Processes

Dual-function catalytic processes use an acidic oxide support, such as alumina, loaded with a metal such as Pt to isomerize the xylenes as well as convert EB to xylenes. These catalysts promote carbonium ion-type reactions as well as hydrogenation–dehydrogenation. In the mechanism for the conversion of EB to xylenes shown, EB is converted to xylenes



by hydrogenation of the aromatic ring and formation of naphthenic intermediates such as ethylcyclohexane, dimethylcyclohexanes, and trimethylcyclohexanes. To provide an effective pathway between EB and xylenes, a certain concentration of the naphthenic intermediates must be maintained. This is accomplished by proper selection of operating conditions and separation and recycle of the naphthenic intermediates. Side reactions include disproportionation and hydrodealkylation of aromatic compounds, and hydrodealkylation of naphthenes. Effective catalysts minimize the loss of xylenes and EB via these side reactions.

Commercial processes which use a dual-functional catalyst are Octafining, Isomar, and Isolene.

The Octafining process (114–116) was developed and commercialized by Atlantic Richfield and Engelhard in the early 1960s. The first-generation catalyst was prepared by mixing equal amounts of a silica–alumina cracking catalyst with Pt on alumina. The Pt content of the mixture was about 0.5 wt %. The EB approach to equilibrium was 88%, with an 80% selectivity to xylenes. Reaction conditions consist of temperature of 425–480°C; pressure of 1.14–2.51 MPa; H_2/hydrocarbon ratio $< 10:1$ (preferably 4–6:1); and $\mathrm{LHSV} = 0.6 - 1.6/\mathrm{h}$. An equilibrium mixture of xylenes is produced. To maintain conversion, the reaction temperature is gradually increased as the catalyst deactivates up to a maximum temperature of about 480°C. The catalyst is then regenerated. The first Octafining unit was placed onstream in 1960. As of 1995, 30 units had been licensed in 17 countries (99).

Recently, a new second-generation catalyst has been commercialized. This new catalyst, O-750, is formulated by loading Pt on alumina and combining the mixture with H–mordenite such that the final Pt content is <0.5 wt% (101). This catalyst, along with several other process improvements, forms the basis of the Octafining II process. Compared to Octafining I, yields and per pass conversions have been improved. Catalyst cycle lengths typically exceed 3 yr. The catalyst is capable of cracking C_9 nonaromatics, thereby increasing xylene purity. IFP has recently acquired the rights to license the Octafining II process worldwide (99).

UOP's Isomar process (56, 117–119) was originally developed to use dual-functional catalysts. The first-generation catalyst contained Pt and halogen on alumina. Operating conditions using this catalyst were 399°C; 1.25 MPa; 2 LHSV; and H_2/hydrocarbon ratio of 6:1. A C_8 naphthene concentration of 2–9% was maintained in the process loop. In the mid-1980s UOP introduced an improved catalyst, I-9. Unlike the original catalyst, this catalyst does not require chlorine addition. Process conditions were modified to 388°C and 1.68 MPa.

In 1993, UOP commercialized an improved Pt-based catalyst, I-210. This catalyst is based on a molecular sieve, but not an aluminosilicate zeolite. UOP claims that yields are about 10% better than those for I-9 catalyst. EB to xylenes conversion is about 22–25% with a C_8 aromatics per pass loss of about 1.2–1.5%. As discussed below, UOP's Isomar process can also use zeolite catalysts which convert EB to benzene rather than to xylenes. UOP has licensed over 40 Isomar units.

The Isolene II process was commercialized in 1971 by Toray Industries (120–122). The catalyst is Pt on an acidic support. Operating conditions are reported to be 250–500°C and 1–3 MPa. The first Isolene II plant was built at Toray's Kawasaki complex.

4.5.2. Zeolite and Molecular Sieve-Based Process

Mobil has commercialized several xylene isomerization processes that are based on ZSM-5. Amoco has developed a process based on a medium-pore borosilicate molecular sieve.

Mobil's Low Pressure Isomerization Process (MLPI) was developed in the late 1970s (123, 124). Two unique features of this process are that it is operated at low pressures and no hydrogen is used. In this process, EB is converted to benzene and diethylbenzene via disproportionation. The patent believed to be the basis for the MLPI process (123) discusses the use of H-ZSM-5 zeolite with an alumina binder. The reaction conditions described are start-of-run temperatures of 290–380°C, a pressure of 273 kPa; and WHSV of 5–8.5/h. The EB conversion is about 25–40% depending on reaction conditions, with xylene losses of 2.5–4%. The PX approach to equilibrium is about 99–101%. The first commercial unit was licensed in 1978. A total of four commercial plants have been built.

A second Mobil process is the Mobil's Vapor Phase Isomerization Process (MVPI) (125, 126). This process was introduced in 1973. Based on information in the patent literature (125), the catalyst used in this process is believed to be composed of NiHZSM-5 with an alumina binder. The primary mechanism of EB conversion is the disproportionation of two molecules of EB to one molecule of benzene and one molecule of diethylbenzene. EB conversion is about 25–40%, with xylene losses of 2.5–4%. PX is produced at concentration levels of 102–104% of equilibrium. Temperatures are in the range of 315–370°C, pressure is generally 1480 kPa, the H_2/hydrocarbon molar ratio is about 6:1, and WHSV is dependent on temperature, but is in the range of 2–50, although normally it is 5–10.

Mobil's High Temperature Isomerization (MHTI) process, which was introduced in 1981, uses Pt on an acidic ZSM-5 zeolite catalyst to isomerize the xylenes and hydrodealkylate EB to benzene and ethane (126). This process is particularly suited for unextracted feeds containing C_{8+} aliphatics, because this catalyst is capable of cracking them to light paraffins. Reaction occurs in the vapor phase to produce a PX concentration slightly higher than equilibrium, ie, 102–104% of equilibrium. EB conversion is about 40–65%, with xylene losses of about 2%. Reaction conditions are temperature of 427–460°C, pressure of 1480–1825 kPa, WHSV of 10–12, and a H_2/hydrocarbon molar ratio of 1.5–2:1. Compared to the MVPI process, the MHTI process has lower xylene losses and lower formation of heavy aromatics.

In the early 1990s, Mobil commercialized their High Activity Isomerization (MHAI) process (124, 127, 128). A patent corresponding to this process (127) describes the use of a two catalyst system in which the catalyst beds are separated from each other but can be located in the same reactor. The first catalyst consists of a noble metal (preferably Pt) on ZSM-5 zeolite having a crystal size of at least 1 micron with an alpha value >100. The primary function of this catalyst is to hydrodealkylate the EB to benzene and ethane. The second catalyst consists of a noble metal, preferably Pt, on a ZSM-5 zeolite having a crystal size <1 micron and an alpha value <100. The primary function of this catalyst is to isomerize the xylenes. Preferred operating conditions are reported to be 400–480°C; 450–2860 kPa, WHSV of 3–50; and a H_2/hydrocarbon molar ratio of 1–5:1. For a nonextracted feed containing 15% EB, typical EB conversions are 65%, with xylene losses of 1.8%. Compared to MHTI, for a given EB conversion MHAI xylene losses are lower and nonaromatics conversion higher. As of 1995, 9 MHAI units had been commercialized (127).

Amoco has developed a series of xylene isomerization catalysts called AM-SAC catalysts (129). These catalysts are based on a medium-pore borosilicate molecular sieve, designated AMS-1B. They are reported to retard xylenes destruction by suppressing the transfer of methyl groups. Amoco claims that the required intermediate is too bulky to form within the pores of AMS-1B. EB is reacted via transfer of ethyl groups in a reaction scheme that involves dealkylation, formation of ethylene, and realkylation. Optionally, a hydrogenating metal such as Pt is added to inhibit realkylation by intercepting the ethylene and converting it to ethane, which is essentially unreactive. This has the advantage of further limiting xylene losses by preventing the alkylation of xylenes with C_2 groups to ethyl methyl benzenes. Amoco claims to have used its AMSAC catalysts in its PX units since 1980.

4.5.3. Amorphous Silica–Alumina Based Processes

Amorphous silica–alumina catalysts had been used for many years for xylene isomerization. Examples are the Chevron (130), Maruzen (131), and ICI (132–135). The primary advantage of these processes was their simplicity. No hydrogen was required and the only side reaction of significance was disproportionation. However, in the absence of H_2, catalyst deactivation via coking was rapid and regeneration was required every 3–30 days. Swing reactors were used to permit operation to continue during catalyst regenerations. The volume of catalyst used was fairly large, although the catalyst was inexpensive. Losses via disproportionation tended to be high, up to 5–10% xylene and 10–15% EB per pass under conditions at which xylenes were isomerized to near-equilibrium values. PX was produced at concentrations of 95–100% of equilibrium.

Freshly regenerated catalyst was brought onstream at 370–420°C and temperature was gradually increased to maintain a $>95\%$ approach to equilibrium. The cycle length depended on feed and was longer when the OX concentration in the feed was low. The catalysts were very stable to regeneration by burnoff of coke and typically lasted several years before needing to be replaced. Generally, the catalyst activity loss was the result of a decrease in surface area which occurred slowly at regeneration conditions.

The ICI process was used in four U.K. plants and plants in Poland, Japan, and the former Soviet Union. This process operated without any feed diluent and the catalyst could undergo at least one rejuvenation *ex situ*. The temperature operating range was 430–450°C, with carbon deposition increasing rapidly at higher temperatures. Cycle lengths tended to be three to four days before regeneration. In most instances, EB was rejected from the fresh feed although concentrations of 20–25% could be tolerated. The feed rate was about 0.5/h LHSV over that of a compressed pellet catalyst.

The Chevron processwas used in two U.S. plants, although it is no longer used. Cycle lengths ranged from 6–30 d, depending on catalyst age and OX content of the feed. Operating conditions were temperature of 370–470°C and space velocity of about 0.5/h. Addition of 5 wt % steam reduced disproportionation losses.

5. Economic Aspects

Worldwide capacities as of 1992 for the production of the C_8 aromatic isomers are summarized in Table 6. U.S. capacity and production figures are given in Table 7.

U.S. producers and capacities for PX, OX, and EB are summarized in Table 8. Amoco is the only producer of MX with an annual capacity of 110,000 t. In recent years, many small xylene plants have shut down because the operations were not economic or the technology being used was obsolete.

The price histories for the four isomers are given in Reference 1. The average values started to increase drastically in late 1973 owing to increases in world crude oil prices. They also increased sharply from 1979–1985 in response to increased crude oil prices and shortages of xylenes. From 1986–1992 the prices generally declined as availability increased and crude oil prices declined, except in 1989 when derivatives demand was strong and xylenes supply was tight.

Table 6. Worldwide Capacity for C_8 Aromatic Isomers in 1995,[a] 10^3 t

Location	OX	PX	MX	EB
United States	508	3,244	110	5,944
Canada and Mexico	122	608	0	1,104
Western Europe	665	1,310	0	5,157
Eastern Europe	674	852	0	1,841
Japan	302	2,200	55	3,587
other Asia	503	3,306	0	2,644
other	282	438	0	1,158
Total	*3,056*	*11,958*	*165*	*21,435*

[a] Ref. 136.

Table 7. U.S. Xylenes Economic Data in 1995,[a] 10^3 t

Parameter	Mixed xylenes	OX	MX	PX
production	4290	460	98	2877
imports	448	41	5	296
exports	616	78	32	615
consumption	4122	423	71	2558
OX	460			
MX	98			
PX	3452			
phthalic anhydride		363		
isophthalic acid			61	
dimethyl terephthalate				745
terephthalic acid				1743
other	112	60	8	70
year-end capacity	6140	508	110	3244
production/capacity	0.70	0.91	0.89	0.89

[a] Ref. 137.

6. Analytical Methods

Typical ASTM methods for analyzing the C_8 aromatic isomers are listed in Table 9.

p-Xylene purities can be determined by both freezing point and chromatographic methods. One advantage of freezing point methods is that they can detect the presence of water and carbon dioxide impurities, which chromatographic methods do not. Chromatographic methods exhibit another disadvantage, ie, for the analysis of very high purity PX streams, in that the PX peak tends to tail over the MX peak. Conditions for one chromatographic method for separating C_8 aromatic isomers are given in Table 10. This procedure readily separates benzene, toluene, and the C_8 aromatic isomers. Di-*n*-propyl tetrachlorophthalate is also a useful column coating because it reverses the positions of PX and MX. Thus, in the case of this column, MX elutes ahead of PX and provides better analysis for streams containing high purity PX.

Bentone-34 has commonly been used in packed columns (138, 139). The retention indices of many benzene homologues on squalane have been determined (140). Gas chromatography of C_6–C_{11} aromatic compounds using a Ucon B550X-coated capillary column is discussed in Reference 141. A variety of other separation media have also been used, including phthalic acids (142), liquid crystals (143), and Werner complexes (144). Gel permeation chromatography of alkylbenzenes and the separation of the C_8 aromatics treated with zeolites are described in References (145–148).

Table 8. U.S. Capacity for PX, OX, and EB, 1995,[a] 10^3 t

		Xylene process				
Company	Location	Separation[b]	Isomerization	PX	OX	EB
Amoco	Decatur, Ala.	Amoco	Amoco	651		
	Texas City, Tex.	Amoco	Amoco	685		412
Arco	Channelview, Tex.					1,265
Chevron	Pascagoula, Miss.	Chevron	Mobil	242		
	St. James, La.					771
CosMar	Carville, La.					998
Dow	Freeport, Tex.					794
Exxon	Baytown, Tex.	Parex[c]	Mobil	454	127	
Huntsman	Bayport, Tex.					562
Koch	Corpus Christi, Tex.	Parex[c]	Mobil	590	125	
Lyondell	Houston, Tex.	Arco	Mobil	181	109	
Mobil	Chalmette, La.	Amoco	Mobil	70	70	
Phillips	Guayama, P.R.	Parex[c]	Mobil	371	77	
Rexene	Odessa, Tex.					159
Sterling	Texas City, Tex.					816
Westlake	Lake Charles, La.					167
Total				*3,244*	*508*	*5,944*

[a] Ref. 136.
[b] Crystallization process, unless otherwise noted.
[c] Adsorption process.

Table 9. Analytical Methods for C_8 Aromatic Isomers

Assay	ASTM method
purity, mol %	D1016
distillation range, °C	D850
specific gravity, 15.5°C/15.5°C	D891
color Saybolt	D156
flash point, °C	D56

7. Health and Safety Factors

The xylene isomers are flammable liquids and should be stored in approved closed containers with appropriate labels and away from heat and open flames. Limits for transportation by air are 5 L on passenger planes and 60 L on cargo planes.

Flash points and autoignition temperatures are given in Table 11. The vapor can travel along the ground to an ignition source. In the event of fire, foam, carbon dioxide, and dry chemical are preferred extinguishers. The lower and upper explosion limits are 1% and 7%.

The xylenes are mildly toxic. They are mild skin irritants, and skin protection and the cannister-type masks are recommended. The oral LD_{50} value for rats is 4300 ppm. The STEL for humans is 150 ppm. Xylenes show only mild toxicity to fish, and the threshold limit for crop damage is 800–2400 ppm. Biodegradation with activated seed is slow, and sewage digestion is impaired by 0.1% concentrations. In the event of a spill, oil-skimming equipment, adsorbent foam, and charcoal may be used for cleanup.

Table 10. Chromatographic Separation of C_8 Aromatic Isomers

Parameter	Value or measure
column[a]	30.5 m × 0.5 mm dia
sample size, microliter	0.2
detector	flame ionization
temperature, °C	70
pressure, kPa (psig)	156 (8)
helium flow, mL/min	8

[a] Stainless steel column coated with *m*-bis(*m*-phenoxyphenoxy)benzene.

Table 11. Flash Points and Autoignition Temperatures of the C_8 Aromatic Compounds

Compound	Flash point, °C	Autoignition temperature, °C
PX	27	530
MX	27	530
OX	32	460
EB	15	432

8. Uses

The majority of xylenes, which are mostly produced by catalytic reforming or petroleum fractions, are used in motor gasoline (see Gasoline and other motor fuels). The majority of the xylenes that are recovered for petrochemicals use are used to produce PX and OX. PX is the most important commercial isomer. Almost all of the PX is converted to terephthalic acid and dimethylterephthalate, and then to poly(ethylene terephthalate) for ultimate use in fibers, films, and resins.

Almost all of the OX that is recovered is used to produce phthalic anhydride. Phthalic anhydride is a basic building block for plasticizers used in flexible PVC resins, for polyester resins used in glass-reinforced plastics, and for alkyd resins used for surface coatings. OX is also used to manufacture phthalonitrile, which is converted to copper phthalocyanine, a pigment.

Most of the MX that is contained in recovered mixed xylenes is isomerized to PX and OX. MX is also used to produce isophthalic acid and isophthalonitrile. Isophthalic acid is the base of unsaturated polyester resins which have good corrosion resistance, and greater strength and higher modulus than resins derived from phthalic anhydride. Isophthalonitrile is the starting material for the fungicide tetrachloroisophthalonitrile.

Some of the mixed xylenes that are produced are used as solvents in the paints and coatings industry (see Solvents, industrial). However, this use has declined, particularly in the United States as environmental efforts to reduce hydrocarbon emissions into the air have increased.

The EB present in recovered mixed xylenes is largely converted to xylenes or benzene. The EB used to make styrene is predominately manufactured by the alkylation of benzene with ethylene.

BIBLIOGRAPHY

"Xylenes and Ethylbenzene" in *ECT* 1st ed., Vol. 15, pp. 186–194, by M. Lapeyrouse, Esso Research and Engineering Co.; in *ECT* 2nd ed., Vol. 22, pp. 467–507, by H. E. Cier, Esso Research and Engineering Co.; in *ECT* 3rd ed., Vol. 24, pp. 709–744, by D. L. Ransley, Chevron Research Co.

Cited Publications

1. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1993.
2. C. L. Yaws, *Chem. Eng.*, 113 (July 21, 1975).
3. C. L. Yaws, *Chem. Eng.*, 73 (Sept. 29, 1975).
4. J. Chao and co-workers, *Hydrocarbon Process.* **59** (8), 117 (1980).
5. J. Chao, *Hydrocarbon Process.* 295 (Nov. 1979).
6. D. R. Stull and co-workers, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, 1968.
7. W. L. Nelson, *Oil Gas J.*, 68 (Mar. 19, 1970).
8. D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.* **74**, 6246 (1950).
9. H. C. Brown and H. Jungk, *J. Am. Chem. Soc.* **77**, 5579 (1955).
10. R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.* **81**, 5289 (1959).
11. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, API Research Project 44, Carnegie Press, 1953.
12. W. D. Crow and C. Wentrup, *Tetrahedron Lett.* **27**, 3111 (1968).
13. C. J. Egan, *J. Chem. Eng. Data* **5**(3), 298 (1960).
14. S. Ehrenson, *J. Am. Chem. Soc.* **84**, 2681 (1962).
15. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.* **73**, 2013 (1951).
16. M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.* **75**, 577 (1953).
17. E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 186 (1958).
18. J. Barnard and B. M. Sankey, *Combust. Flame* **12**(4), 345 (1968).
19. L. Errede and M. Swarc, *Q. Rev.* **12**, 301 (1958).
20. L. Errede, R. Gregorian, and J. Hoyt, *J. Am. Chem. Soc.* **82**, 5218 (1960).
21. L. Errede and N. Kroll, *J. Polym. Sci.* **60**, 33 (1962).
22. U.S. Pat. 3,412,167 (Nov. 19, 1968), J. W. Lewis, (to Union Carbide Co.).
23. D. J. Hadley, *Chem. Ind.*, 238 (Feb. 25, 1961).
24. *Hydrocarbon Process.*, 252 (Nov. 1969).
25. *Hydrocarbon Process.*, 238 (Nov. 1981).
26. E. Kamegaya, *Chem. Econ. Eng.* **2**(2), 30 (1970).
27. S. Ariki and A. Ohira, *Chem. Econ. Eng.* **5**(7), 39 (1973).
28. N. E. Ockerbloom, *Hydrocarbon Process.*, 101 (Feb. 1972).
29. P. B. de la Mare and J. Robertson, *J. Chem. Soc.*, 279 (1943).
30. F. Condon, *J. Am. Chem. Soc.* **70**, 1963 (1948).
31. U.S. Pat. 2,282,231 (May 5, 1942), W. J. Mattox (to UOP).
32. O. Maas and J. Russell, *J. Am. Chem. Soc.* **40**, 1561 (1918).
33. O. Maas, E. H. Boomer, and D. M. Morrison, *J. Am. Chem. Soc.* **45**, 1433 (1923).
34. H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.* **74**, 191 (1952).
35. W. D. Schaeffer and W. S. Dorsey, *Advances in Petroleum Chemistry and Refining*, Vol. **6**, Wiley-Interscience, New York, 1962.
36. W. D. Schaeffer and co-workers, *J. Am. Chem. Soc.* **79**, 5870 (1957).
37. U.S. Pat. 2,798,103 (July 2, 1957) and U.S. Pat. 2,951,104 (Aug. 30, 1960), W. D. Schaeffer and J. D. Wordie (to Union Oil Co.).
38. M. J. Minton and co-workers, *J. Phys. Chem.* **71**(11), 3618 (1967).
39. J. Menyhart, *Magy. Kem. Lapja* **22**(1), 18 (1967).

40. F. Casellato, *Erdoel Kohle* **22**, 2 (1969).
41. E. Ger. Pat. 56,236 (June 6, 1967), W. Jugel.
42. Brit. Pat. 1,151,606 (May 14, 1969), J. Lumsden (to Imperial Smelting Co.).
43. H. R. Allcock and L. A. Siegel, *J. Am. Chem. Soc.* **86**, 5140 (1964).
44. U.S. Pat. 3,472,762 (Oct. 14, 1969), A. Goldrup and M. T. Westaway (to British Petroleum).
45. U.S. Pat. 3,484,500 (Dec. 16, 1969), A. Goldrup, A. B. Morrison, and M. T. Westaway (to British Petroleum).
46. Brit. Pat. 1,183,524 (Mar. 11, 1970) (to British Petroleum Co.).
47. U.S. Pat. 3,504,047 (Mar. 31, 1970), J. N. Haresnape (to British Petroleum Co.).
48. U.S. Pat. 3,456,028 (July 15, 1969), C. G. Gerhold and D. B. Broughton (to UOP).
49. U.S. Pat. 3,465,055 (Sept. 2, 1969), W. K. T. Gleim, R. C. Wackler, and R. C. Ranquist (to UOP).
50. U.S. Pat. 2,900,428 (Aug. 18, 1959), C. D. Heaton and W. E. Toland (to Chevron Research Co.).
51. U.S.S.R. Pat. 176,277 (Nov. 2, 1965), V. S. Bogdanov and co-workers (to Scientific Research Institute for Petrochemical Industries).
52. C. J. Egan and R. V. Luthy, *Ind. Eng. Chem.* **47**, 250 (1955).
53. T. Iwamura, S. Otani, and M. Sato, *Bull. Jpn. Pet. Inst.* **13**(1), 116 (1971).
54. S. Otani, *Chem. Eng.*, 118 (July 20, 1970).
55. *Hydrocarbon Process.*, 133 (Nov. 1977).
56. UOP Petrochemical Technology Conference, 1992, Houston, Tex.
57. J. J. Jeanneret, in R. A. Meyers, ed., *Handbook of Petroleum Refining Processes*, 2nd ed., McGraw-Hill Book Co., Inc., New York, 1997, p. 2.55.
58. J. A. Verdol, *Oil Gas J.*, 63 (June 9, 1969).
59. HRI/IFP Petrochemical Seminar, May 8–9, 1995, Houston, Tex.
60. P. Grandio and F. H. Schneider, *Oil Gas J.*, 62 (Nov. 29, 1971).
61. P. Grandio and co-workers, *Hydrocarbon Process.* **51**, 85 (Aug. 1972).
62. S. Han, and co-workers, *Oil Gas J.*, 83 (Aug. 21, 1989).
63. Brochure on MTDP-3, Mobil Oil Corp., 1996.
64. F. Gorra, L. Breckeridge, R. Sailor, *Oil Gas J.* **90**(41), 60 (Oct. 12, 1992).
65. R. Sailor, presentation at Chiyoda Forum, Saudi Arabia, 1993.
66. Brochure on MSTDP, Mobil Oil Corp., 1996.
67. D. Rothman, *Chem. Week*, 18 (Aug. 30/Sept. 6, 1995).
68. U.S. Pat. 5,243,117 (Sept. 7, 1993), C. D. Chang and D. S. Shihabi (to Mobil Oil Corp.).
69. Technical data, Mobil Technology Sales and Licensing, (Mobil Oil Co., May, 1996.
70. K. Menard, *Oil Gas J.*, 46 (Mar. 16, 1987).
71. U.S. Pat. 3,467,724 (Sept. 16, 1969), S. A. Laurich (to Chevron Research Co.).
72. *Hydrocarbon Process.*, 253 (Nov. 1979).
73. U.S. Pat. 3,177,265 (Apr. 6, 1965), G. C. Lammens, (to Standard Oil Co., Indiana).
74. Belg. Pat. 617,795 (Sept. 14, 1962), (to Standard Oil Co., Indiana).
75. R. J. Desiderio and co-workers, *Hydrocarbon Process.*, **53**(8), 81 (1974).
76. *Hydrocarbon Process.*, 239 (1981).
77. Y. Hatanaka and T. Nakamura, *Oil Gas J.* **70**(47), 60 (1972).
78. *Hydrocarbon Process.*, 254 (Nov. 1979).
79. D. L. McKay and H. W. Goard, *Chem. Eng. Prog.* **61**(11), 99 (1966).
80. D. L. McKay and co-workers, *Chem. Eng. Prog.* **62**(11), 104 (1966).
81. *Hydrocarbon Process.*, 132 (Mar. 1995).
82. G. Parkinson, *Chem. Eng.* **103**(9), 23 (Sept. 1996).
83. N. P. Wynn, *Chem. Eng. Prog.* **88**(3), 52 (1992).
84. D. B. Broughton and co-workers, *The Separation of p-Xylene from* C_8 *Hydrocarbon Mixtures by Parex Process*, AIChE, Puerto Rico, May 1970.
85. D. B. Broughton and co-workers, *Chem. Eng. Prog.* **66** (9), 70 (1970).
86. D. P. Thornton, Jr., *Hydrocarbon Process.*, 151, (Nov. 1970).
87. D. B. Broughton, *Chem. Eng. Prog.* **73**(10), 49 (1977).
88. *Hydrocarbon Process.*, 256 (Nov. 1979).

89. U.S. Pat. 3,663,638 (May 16, 1972), R. W. Neuzil (to UOP).
90. U.S. Pat. 3,665,046 (May 23, 1972), A. J. DeRosset (to UOP).
91. U.S. Pat. 3,686,342 (Aug. 22, 1972), R. W. Neuzil (to UOP).
92. U.S. Pat. 3,636,180 (Jan. 18, 1972), D. B. Broughton (to UOP).
93. U.S. Pat. 3,696,107 (Oct. 3, 1972), R. W. Neuzil (to UOP).
94. Ref. 57, p. 2.45.
95. S. Otani and co-workers, *Chem. Econ. Eng. Rev.*, 56 (June 1971).
96. S. Otani, *Chem. Eng.*, 106 (Sept. 17, 1973).
97. S. Otani and co-workers, *Jpn. Pet. Inst. Bull.* **16**(1), 60 (1974).
98. U.S. Pat. 3,761,533 (Sept. 25, 1973), S. Otani and co-workers (to Toray Industries, Inc.).
99. G. Ash and co-workers, *Rev. de IFP* **49**(5), 541 (Sept.–Oct. 1994).
100. M. Seko, *Oil Gas J.*, 81 (July, 1979).
101. M. Seko, T. Miyake, and K. Inada, *IEC Prod. Res. Dev.* **18** (4), 263 (1979).
102. M. Seko, T. Miyake, and K. Inada, *Hydrocarbon Process.*, 133 (Jan. 19, 1980).
103. M. Seko, H. Takeuchi, and T. Inada, *IEC Prod. Res. Dev.* **21**, 656 (1982).
104. Y. Igarashi and T. Ueno, *A New Xylene Separation Process*, ACS Meeting, Atlantic City, N.J., 1968.
105. *Hydrocarbon Process.*, 254 (Nov. 1969).
106. Y. Igarashi, *Jpn. Chem. Q.* **IV**(4), 27 (1969).
107. T. Ueno, *Bull. Jpn. Pet. Inst.* **12** (May 1970).
108. G. R. Herrin and E. H. Martel, *Pet. Petrochem. Int.* **12**(7), 74 (1972).
109. J. C. Davis, *Chem. Eng.*, 77 (Aug. 9, 1971).
110. T. Ueno and T. Nakana, *Eighth World Pet. Congr. Proc.* **4**, 187 (1971).
111. S. Ariki and A. Ohira, *Chem. Econ. Eng. Rev.* **5**(7), 30 (1973).
112. J. J. H. Masseling, *Chem. Tech.*, 714 (Nov. 1976).
113. *Hydrocarbon Process.*, 255 (Nov. 1979).
114. H. F. Uhlig and W. C. Pfefferle, *Am. Chem. Soc. Div. Pet. Chem. D*, 154 (Sept. 1969).
115. P. M. Pitts, Jr., J. E. Connor, Jr., and L. N. Leum, *Ind. Eng. Chem.* **47**(4), 770 (1955).
116. U.S. Pat. 2,976,332 (Mar. 21, 1961), L. N. Leum and J. E. Connor, Jr., (to Atlantic Refining Co.).
117. C. V. Berger, *Hydrocarbon Process.*, 173 (Sept. 1973).
118. *Hydrocarbon Process.*, 215 (Mar. 1993).
119. Ref. 57, p. 2.37.
120. S. Otani and co-workers, *Chem. Econ. Eng. Rev.*, 56 (June 1971).
121. S. Otani, *Chem. Eng.*, 106 (Sept. 17, 1973).
122. Y. Tsuchiya and co-workers, *Jpn. Pet. Inst. Bull.* **16**(1), 60 (1974).
123. U.S. Pat. 4,101,596 (July 18, 1978), K. M. Mitchell and J. J. Wise (to Mobil Oil Corp.).
124. Brochure on MHAI and MLPI, Mobil Oil Corp., 1996.
125. U.S. Pat. 3,856,872 (Dec. 24, 1974), R. A. Morrison (to Mobil Oil Corp.).
126. N. Y. Chen, W. E. Garwood, F. G. Dwyer, *Shape Selective Catalysis in Industrial Applications*, Marcel Dekker, Inc., New York, 1989.
127. U.S. Pat. 4,899,011, (Feb. 6, 1990), Chu and co-workers (to Mobil Oil Corp.).
128. Y. Y. Huang and co-workers, **30d**, 1991 AIChE Spring National Meeting, Houston, Apr. 7–11, 1991.
129. J. Amelse and co-workers, **33a**, *1988 AIChE Summer National Meeting*, Denver, Aug. 21–24, 1988.
130. H. C. Ries, *Process Economics Program 25A*, Stanford Research Institute, Menlo Park, California, July 1970, 41–53.
131. *Hydrocarbon Process.*, 240 (Nov. 1981).
132. *Hydrocarbon Process.*, 109 (Aug. 1969).
133. *Hydrocarbon Process.*, 253 (Nov. 1969).
134. U.S. Pat. 3,793,384 (Feb. 19, 1974), J. G. Chenoweth and co-workers (to Imperial Chemical Industries).
135. U.S. Pat. 3,860,668 (Jan. 14, 1975), J. K. January and A. Marchant (to Imperial Chemical Industries).
136. *World Petrochemicals*, SRI International, Menlo Park, Calif., 1996.
137. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1996.
138. J. M. Vergnaud, *J. Chromatogr.* **27**, 54 (1967).
139. C. F. Raley and J. W. Kaufman, *Anal. Chem.* **40**(8), 1371 (1968).

140. M. Dimov and D. Papzova, *J. Chromatogr.* **137**, 265 (1977).
141. F. Baumann and S. M. Csicsery, *J. Chromatogr.* **26**, 262 (1967).
142. M. F. Burke and L. B. Rogers, *J. Chromatogr. Sci.* **6**(1), 75 (1968).
143. A. B. Richmond, *J. Chromatogr. Sci.* **9**(9), 571 (1971).
144. A. C. Bhattacharyya and A. Bhattacherjee, *J. Chromatogr.* **41**(3–4), 446 (1969).
145. M. Popl, J. Coupek, and S. Pokorny, *J. Chromatogr.* **104**, 135 (1975).
146. U.S. Pat. 3,653,184 (Apr. 4, 1972), B. M. Drinkard, P. T. Allen, and E. H. Unger (to Mobil Oil Corp.).
147. U.S. Pat. 3,656,278 (Apr. 18, 1972), B. M. Drinkard, P. T. Allen, and E. H. Unger (to Mobil Oil Corp.).
148. U.S. Pat. 3,724,170 (Apr. 3, 1973), P. T. Allen, B. M. Drinkard, and E. H. Unger, (to Mobil Oil Corp.).

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