TOLUENE

1. Introduction

Toluene [108-88-3], C_7H_8, is a colorless, mobile liquid with a distinctive aromatic odor somewhat milder than that of benzene. The name toluene derives from a natural resin, balsam of Tolu, named for a small town in Colombia, South America. Toluene was discovered among the degradation products obtained by heating this resin.

Prior to World War I, the main source of toluene was coke ovens. At that time, trinitrotoluene (TNT) was the preferred high explosive and large quantities of toluene were required for its manufacture (see EXPLOSIVES AND PROPELLANTS). To augment the supply, toluene was obtained for the first time from petroleum sources by subjecting narrow-cut naphthas containing relatively small amounts of toluene to thermal cracking. The toluene concentrate so produced was then purified and used for the manufacture of TNT. Production from petroleum was discontinued shortly after World War I. Petroleum again became the source for toluene with the advent of catalytic reforming and the need for large quantities of toluene for use in aviation fuel during World War II. Since then, manufacture of toluene from petroleum sources has continued to increase, and manufacture from coke ovens and coal-tar products has continued to decrease.

Toluene is generally produced along with benzene, xylenes, and C_9-aromatics by the catalytic reforming of C_6–C_9 naphthas. The resulting crude reformate is extracted, most frequently with sulfolane or tetraethylene glycol and a cosolvent, to yield a mixture of benzene, toluene, xylenes, and C_9-aromatics, which are then separated by fractionation. There have been recent technological developments to produce benzene, toluene, and xylenes from pyrolysis of light hydrocarbons C_2–C_5, LPG, and naphthas (see XYLENES AND ETHYLBENZENE). The majority of the toluene produced annually in the United States is not isolated, but is blended directly into the gasoline pool as a component of reformate and of pyrolysis gasoline. Capacity exists to isolate ca 12.7×10^9 gal per year, which is used for chemicals and solvents. Additional quantities are blended into gasoline to increase octane number.

2. Physical Properties

The physical properties of toluene have been well studied experimentally. Several physical properties are presented in Table 1 (1). Thermodynamic and transport properties can also be obtained, from other sources (2–7). The vapor pressure of toluene can be calculated as follows (8), where P is in kPa and T is in K.

$$\ln P = 14.01 - \frac{3103}{T - 53.36} \quad 310K \leq T \leq 385K \tag{1}$$

The saturated liquid density can be calculated as follows (7), where ρ is in g/L and T is in K.

$$\rho = 12.415 - 0.009548T - \frac{65.155}{606.9 - T} \quad 179K \leq T \leq 400K \tag{2}$$

There is a considerable amount of experimental data for properties of mixtures wherein toluene is a principal constituent. Compilations and bibliographies exist for vapor–liquid equilibrium measurements (9,10), liquid–liquid equilibrium measurements (11), and azeotropic data (12,13).

3. Chemical Properties

Toluene, an alkylbenzene, has the chemistry typical of each example of this type of compound. However, the typical aromatic ring or alkene reactions are affected by the presence of the other group as a substituent. Except for hydrogenation

Table 1. **Physical Properties of Toluene**

Property	Value
molecular weight	92.14
melting point, K	178.15
normal boiling point, K	383.75
critical temperature, K	591.80
critical pressure, MPa[a]	4.108
critical volume, L/(g·mol)	0.316
critical compressibility factor	0.264
acentric factor	0.262
flash point, K	278
autoignition temperature, K	809
Gas properties, 298.15 K	
H_f, kJ/mol[b]	50.17
G_f, kJ/mol[b]	122.2
C_p, J/(mol·K)[b]	104.7
H_{vap}, kJ/mol[b]	38.26
H_{comb}, kJ/mol[b]	−3734
viscosity, mPa·s(= cP)	0.00698
flammability limits, in air[c], vol %	
lower limit at 1 atm	1.2
upper limit at 1 atm	7.1
Liquid properties, 298.15 K	
density, L/mol	9.38
C_p, J/(mol·K)[b]	156.5
viscosity, mPa·s(= cP)	0.548
thermal conductivity, W/(m·K)	0.133
surface tension, mN·m(= dyn/cm)	27.9
Liquid properties, 178.15 K	
density, L/mol	10.49
C_p, J/(mol·K)[b]	135.1
viscosity, mPa·s(= cP)	1.47
thermal conductivity, W/(m·K)	0.162
surface tension, mN·m(= dyn/cm)	42.8
Solid properties	
density at 93.15 K, L/mol	11.18
C_p at 178.15 K, J/(mol·K)[b]	90.0
heat of fusion at 178.15 K, kJ/mol[b]	6.62

[a] To convert MPa to psi, multiply by 145.
[b] To convert J to cal, divide by 4.184.
[c] At 101.3 kPa (1 atm).

and oxidation, the most important reactions involve either electrophilic substitution in the aromatic ring or free-radical substitution on the methyl group. Addition reactions to the double bonds of the ring and disproportionation of two toluene molecules to yield one molecule of benzene and one molecule of xylene also occur.

The aromatic ring has high electron density. As a result of this electron density, toluene behaves as a base, not only in aromatic ring substitution reactions but also in the formation of charge-transfer (π) complexes and in the formation of

Table 2. **Relative Basicity and Reactivity Relative to Toluene = 1.00**

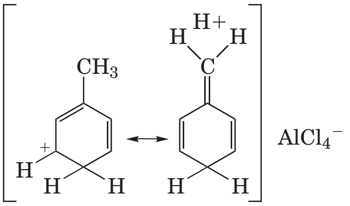
			Xylene		
Electrophile	Benzene	Toluene	*Ortho*	*Meta*	*Para*
Ag^{+a}	0.90	1.00	1.08	1.13	0.98
HCl^{b}	0.66	1.00	1.23	1.37	1.09
TCE[c]	0.54	1.00	1.89	1.62	2.05
$HF\text{-}BF_3{}^{d}$		1.00	200.00	2000.00	100.00
NO_2^{+e}	0.045	1.00			
$Cl_2{}^{f}$	0.003	1.00	13.1	1250.00	6.3

[a] Solubility in aqueous Ag^+ (14).
[b] K for $Ar + HCl \rightleftarrows Ar \cdot HCl$ in *n*-heptane at −78°C (15).
[c] K for association with tetracyanoethylene (TCE) in CH_2Cl_2 (16).
[d] Basicity by competitive protonation (17,18).
[e] CH_3COONO_2 in $(CH_3C)OO$ at 24°C (19).
[f] Cl_2 in CH_3COOH at 24°C (20).

complexes with super acids. In this regard, toluene is intermediate in reactivity between benzene and the xylenes, as illustrated in Table 2.

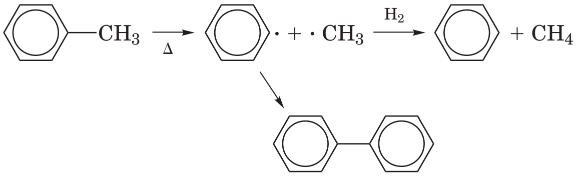
In the formation of π-complexes with electrophiles such as silver ion, hydrogen chloride, and tetracyanoethylene, toluene differs from either benzene or the xylenes by a factor of less than two in relative basicity. This difference is small because the complex is formed almost entirely with the π electrons of the aromatic ring; the inductive effect of the methyl group provides only minor enhancement. In contrast, with HF or BF_3 which form a sigma-type complex, or in the case of reaction as with nitronium ion or chlorine where formation of the sigma bonds and complexes plays a significant role, the methyl group participates through hyperconjugation and the relative reactivity of toluene is enhanced by several orders of magnitude compared to that of benzene. Reactivity of xylenes is enhanced again by several orders of magnitude over that of toluene. Thus, when only the π electrons are involved, toluene behaves much like benzene and the xylenes.

When sigma bonds are involved, toluene is a much stronger base than benzene and a much weaker base than the xylenes. The reasons for this difference are readily shown by contrasting the complexes of toluene with hydrogen chloride in the absence and presence of aluminum chloride. In the absence of aluminum chloride, hydrogen chloride is loosely attached to the π-cloud of electrons above and below the plane of the ring. With aluminum chloride present, the electrophilicity is greatly enhanced and a sigma bond is formed with a specific electron pair; resonance structures involving the methyl group contribute to the stabilization.

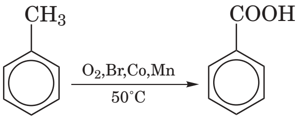


For attack at either of the two ortho positions or the para position, three such structures can be written.

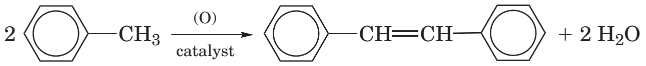
3.1. Hydrogenation Reactions. Hydrogen over a nickel, platinum, or paladium catalyst can partially or totally saturate the aromatic ring. Thermal hyrogenolysis of toluene yields benzene, methane, and biphenyl.



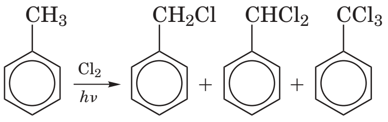
3.2. Oxidation Reactions. Although benzene and methane are quite unreactive toward the usual oxidizing agents, the benzene ring renders the methyl group susceptible to oxidation. With oxygen in the liquid phase and particularly in the presence of catalysts, eg, bromine-promoted cobalt and manganese, very good yields of benzoic acid are obtained.



Partial oxidation of toluene yields stilbene:

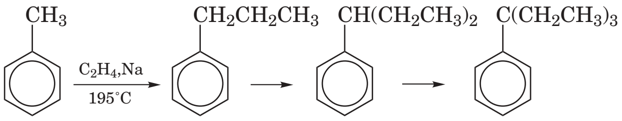


3.3. Substitution Reactions on the Methyl Group. The reactions that give substitution on the methyl group are generally high temperature and free-radical reactions. Thus, chlorination at ca 100°C, or in the presence of ultraviolet light and other free-radical initiators, successively gives benzyl chloride, benzal chloride, and benzotrichloride.



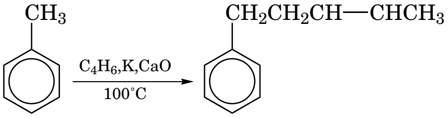
This oxidation reaction which yields benzoic acid is another example of this type of reaction.

In the presence of alkali metals such as potassium and sodium, toluene is alkylated with ethylene on the methyl group to yield, successively, normal propylbenzene, 3-phenylpentane, and 3-ethyl-3-phenylpentane (21).

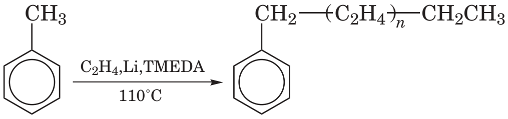


These reactions occur on the benzylic hydrogens because these hydrogens are much more reactive. Competition experiments show, for example, that at 40°C a benzylic hydrogen of toluene is 3.3 times as reactive toward bromine atoms as the tertiary hydrogen of an alkane and nearly 100 million times as reactive as a hydrogen of methane.

In the presence of a potassium catalyst dispersed on calcium oxide, toluene reacts with 1,3-butadiene to yield 5-phenyl-2-pentane (22).

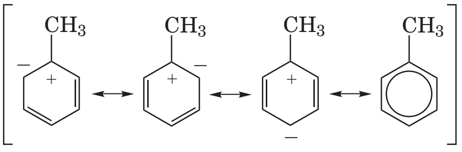


When lithium is used as a catalyst in conjunction with a chelating compound such as tetramethylethylenediamine (TMEDA), telomers are generally obtained from toluene and ethylene (23), where $n = 010$.



The intermediates in these base-catalyzed reactions are believed to be of the nature of a benzyl cation because the reaction product from toluene and propylene is isobutylbenzene, not n-butylbenzene, and the reaction rate is slower than with ethylene (24).

3.4. Substitution Reactions on the Aromatic Ring. To predict the location of electrophilic aromatic ring substitutions, the electrophilic reactions can be modeled as proceeding through an intermediate step in which a negative and positive charge are separated on the ring. The most stable intermediates are those in which the positive charge is localized on the carbon containing the methyl group (tertiary carbon). The resonance structures indicate that substitution will occur at the ortho and para positions but not the meta position because this position cannot be resonance-stabilized by the carbonium–methyl hyperconjugate structures. The presence of the methyl group is therefore ortho- and para-directing. There is also a steric effect at the ortho position, as shown by the data in Table 3. These data clearly demonstrate that bulky groups cannot enter easily into the position adjacent to the methyl group and therefore attack selectively at the para position.



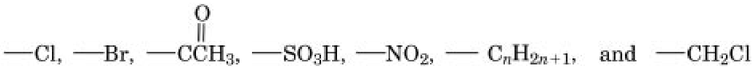
Substitution of the ring hydrogen atoms by electrophilic attack occurs with all of the same reagents that react with benzene. Some of the common groups

Table 3. **Isomer Distributions in the Monoalkylations of Toluene[a], %**

Entering group	Ortho	Meta	Para
methyl	53.8	17.3	28.8
ethyl	45	30	25
isopropyl	37.5	29.8	32.7
t-butyl	0	7	93

[a] Ref. 25.

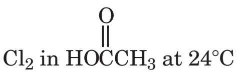
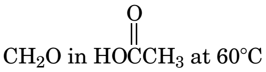
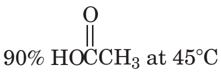
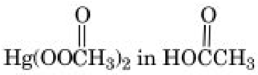
with which toluene can be substituted directly are



$$\mathrm{—Cl,\ —Br,\ —\overset{\overset{O}{\|}}{C}CH_3,\ —SO_3H,\ —NO_2,\ —\ C_nH_{2n+1},\ \ and\ \ —CH_2Cl}$$

Typical electrophilic reactions are summarized in Tables 3 and 4. The reactivity ratios in Table 4 show that under the same conditions, toluene reacts more rapidly than benzene and that those reactions that exhibit the highest selectivity to the ortho and para positions also show the most greatly enhanced reactivity relative to benzene. In addition to these reactions, nitration can be performed with HNO_3 in H_2SO_4, sulfonation can be performed with H_2SO_4

Table 4. **Isomer Distribution and Reactivity Ratio for Selected Reactions[a]**

		Isomer distribution			
Reaction	Conditions	Ortho	Meta	Para	Reactivity ratio
chlorination	 $\mathrm{Cl_2}$ in $\mathrm{HO\overset{\overset{O}{\|}}{C}CH_3}$ at 24°C	58	< 1	42	353
chloromethylation	 $\mathrm{CH_2O}$ in $\mathrm{HO\overset{\overset{O}{\|}}{C}CH_3}$ at 60°C with HCl and $\mathrm{ZnCl_2}$	34.7	1.3	64.0	112
nitration	 90% $\mathrm{HO\overset{\overset{O}{\|}}{C}CH_3}$ at 45°C	56.5	3.5	40.0	24.5
mercuration	 $\mathrm{Hg(OO\overset{\overset{O}{\|}}{C}H_3)_2}$ in $\mathrm{HO\overset{\overset{O}{\|}}{C}CH_3}$ with $\mathrm{HClO_4}$ at 25°C	21.0	9.5	69.5	7.9
sulfonylation	$\mathrm{CH_3SO_2Cl}$ with $\mathrm{AlCl_3}$ at 100°C	49	15	36	
isopropylation	$\mathrm{C_3H_6}$ at 40°C with $\mathrm{AlCl_3}$	37.0	28.5	33.9	2.1

[a] Ref. 25.

and SO_3, alkylation can be performed with RX (X = Cl or Br) with $AlCl_3$, and halogenation can be performed with X_2 (X = Cl or Br) with FeX_3.

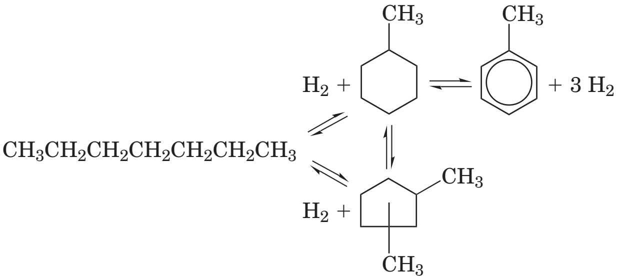
The halogenation reaction conditions can be chosen to direct attack to the methyl group (high temperature or light to form free-radicals) or the aromatic ring (dark, cold conditions with FeX_3 present to form electrophilic conditions).

Toluene itself does not undergo substitution by nucleophilic attack of anions but requires substitution by strongly electronegative groups, such as nitro groups, before the ring becomes sufficiently electrophilic to react with anions.

3.5. Addition Reactions to the Aromatic Ring. Additions to the double bonds in the aromatic ring of toluene result from both free-radical and catalytic reactions. Chlorination using free-radical initiators at temperatures $< 0°C$ saturates the ring. However, this reaction is not entirely selective, for in addition to saturating the ring to yield hexachlorohexane derivatives, the reaction also effects substitution on the methyl group (26). Hydrogenation with typical hydrogenation catalysts readily yields methylcyclohexane. However, rates for hydrogenation of toluene are only 60–70% of that for benzene (27). The commercial technology used for hydrogenating benzene to cyclohexane (28) can be applied directly to the manufacture of methylcyclohexane. Both of these ring-saturating reactions probably proceed stepwise, but since the initial reaction must overcome the high resonance energy of the aromatic ring, saturation of the second and the third double bond is much more rapid, with the result that partially saturated intermediates are not normally detected (29).

4. Manufacture and Processing

The principal source of toluene is catalytic reforming of refinery streams. This source accounts for ca 94% of the total toluene produced. An additional 15% is separated from pyrolysis gasoline produced in steam crackers during the manufacture of ethylene (qv) and propylene (qv). Other sources are an additional 1% recovered as a by-product of styrene manufacture and 4% entering the market via separation from coal tars. The reactions taking place in catalytic reforming to yield aromatics are dehydrogenation or aromatization of cyclohexanes, dehydroisomerization of substituted cyclopentanes, and the cyclodehydrogenation of paraffins. The formation of toluene by these reactions is shown.



Of the main reactions, aromatization takes place most readily and proceeds ca 7 times as fast as the dehydroisomerization reaction and ca 20 times as fast as the dehydrocyclization. Hence, feeds richest in cycloparaffins are most easily reformed. Hydrocracking to yield paraffins having a lower boiling point than feedstock proceeds at about the same rate as dehydrocyclization.

In order to obtain pure aromatics, crude reformate is extracted to separate the aromatics from unreacted paraffins and cycloparaffins. The aromatics are, in turn, separated by simple fractional distillation to yield high purity benzene, toluene, xylenes, and C_9 aromatics.

Catalytic reforming, which was introduced primarily to increase octane values for both aviation and automotive fuels, has since become the main source of benzene and xylenes as well as of toluene. Before 1940, both fixed-bed and fluidized-bed units, typically using a 10–15% Mo–Al_2O_3 catalyst or similar catalysts promoted with 0.5–2% cobalt, predominated. Improved operation was obtained in 1940 by the introduction of a 0.3–0.6% Pt–Al_2O_3 catalyst. Since ca 1970, further improvement has been obtained by promoting the Pt–Al_2O_3 catalyst with up to 1% chloride, by using bimetallic catalysts containing 0.3–0.6% of both platinum and rhenium to retard deactivation, and by using molecular sieves as part of the catalyst base to gain activity. Continuous catalytic reforming was introduced ca 1971.

Because catalytic reforming is an endothermic reaction, most reforming units comprise about three reactors with reheat furnaces in between to minimize kinetic and thermodynamic limitations caused by decreasing temperature. There are three basic types of operations, ie, semiregenerative, cyclic, and continuous. In the semiregenerative operation, feedstocks and operating conditions are controlled so that the unit can be maintained on-stream from 6 mo–2 yr before shutdown and catalyst regeneration. In cyclic operation, a swing reactor is employed so that one reactor can be regenerated while the other three are in operation. Regeneration, which may be as frequent as every 24 h, permits continuous operation at high severity. Since ca 1970, continuous units have been used commercially. In this type of operation, the catalyst is continuously withdrawn, regenerated, and fed back to the system. Flow sheets for representatives of each of the three types of processes, ie, Rheniforming (30), Ultraforming (31), and Platforming (32), are shown in Figures 1, 2, and 3, respectively.

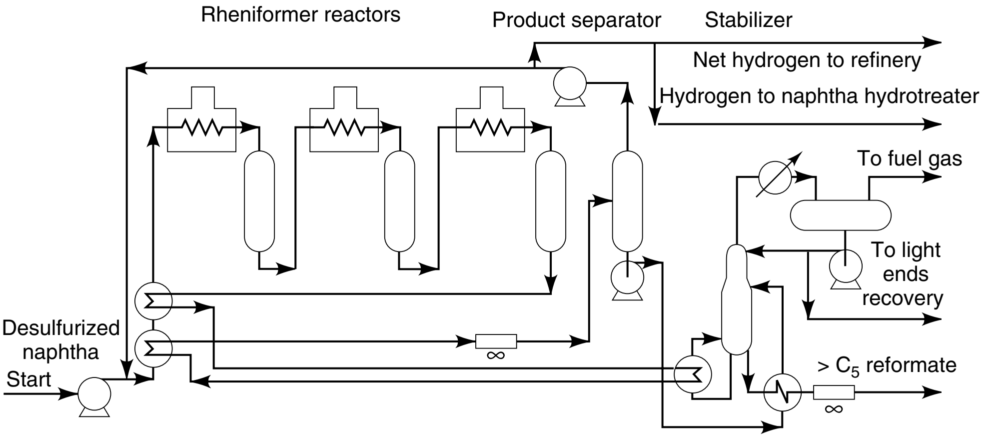


Fig. 1. Chevron Research Co. Rheniforming process (30). (Courtesy of Gulf Publishing Co.)

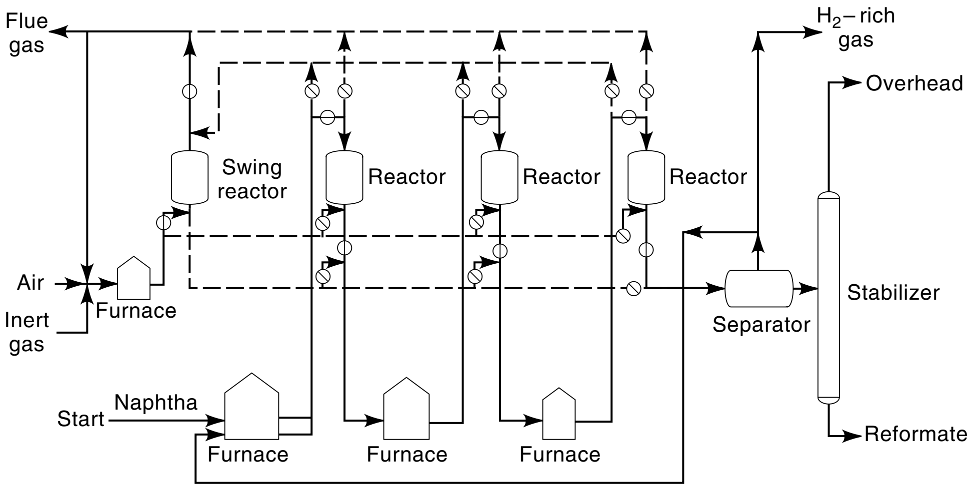


Fig. 2. Standard Oil (In) Co. Ultraforming process (31). (Courtesy of Gulf Publishing Co.)

The predominant feeds for reforming are straight-run naphthas from crude stills. Naphthas from catalyst crackers and naphthas from code stills are also used. Typical compositions are summarized in Table 5. Typical operating conditions for catalytic reforming are 1.135–3.548 MPa (150–500 psi), 455–549°C, 0.356–1.069 m^3 H_2/L (2000–6000 ft^3/bbl) of liquid feed, and a space velocity (wt feed per wt catalyst) of 1–5 h. Operation of reformers at low pressure, high temperature, and low hydrogen recycle rates favors the kinetics and the thermodynamics for aromatics production and reduces operating costs. However, all three of these factors, which tend to increase coking, increase the deactivation rate of the catalyst; therefore, operating conditions are a compromise. More

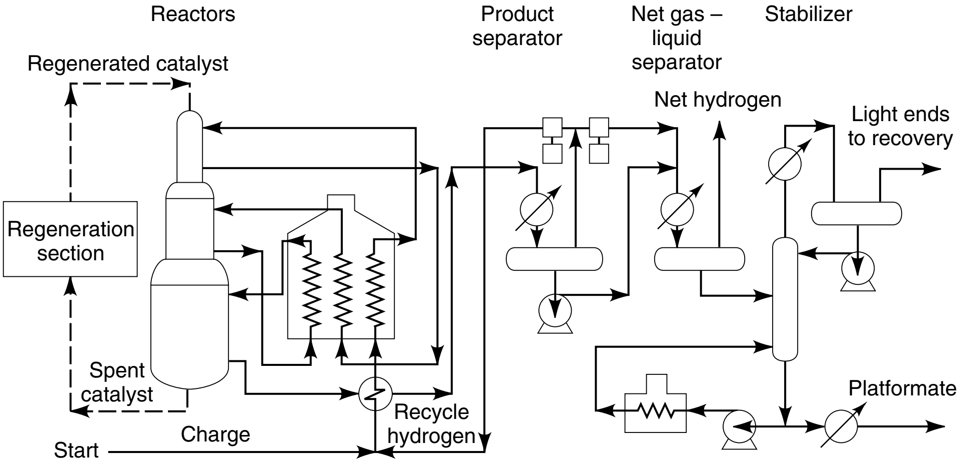


Fig. 3. Universal Oil Products Platforming process (32). (Courtesy of Gulf Publishing Co.)

Table 5. **Composition of Typical 93–204°C Reformer Feeds, Vol %**

Source	Paraffins	Cycloparaffins	Aromatics
crude still	40–55	40–30	10–20
catalytic cracker	30–40	15–25	40–50
coking still	50–55	30–35	10–15

detailed treatment of the catalysis and chemistry of catalytic reforming is available (33–35). Typical reformate compositions are shown in Table 6.

4.1. Toluene, Benzene, and BTX Recovery.

The composition of aromatics centers on the C_7- and C_8-fraction, depending somewhat on the boiling range of the feedstock used. Most catalytic reformate is used directly in gasoline. That part which is converted to benzene, toluene, and xylenes for commercial sale is separated from the unreacted paraffins and cycloparaffins or naphthenes by liquid–liquid extraction or by extractive distillation. It is impossible to separate commercial purity aromatic products from reformates by distillation only because of the presence of azeotropes, although complicated further by the closeness in boiling points of the aromatics, *cyclo*-paraffin, and unreacted C_6-, C_7-, and C_8-paraffins.

Most of the technologies practiced for the recovery of toluene, benzene, and BTX are based on choice of solvent to dissolve the aromatics or nonaromatics in the case of liquid–liquid extraction, or to enhance the relative volatility of the nonaromatics in the case of extractive distillation. UOP and Dow Chemical in the 1950s developed the Udex process, which used glycol-based solvents, ie, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TTEG), dipropylene glycol, and diglycoamine, in a combined liquid–liquid extraction and extractive distillation to extract aromatics from wide boiling range reformates. Next, the Shell-developed sulfolane process also marketed by UOP (Fig. 4) increased the aromatic separation efficiency by using the solvent tetrahydrothiophene dioxide (sulfolane) in a combined liquid–liquid extraction and extractive distillation to dissolve the smaller fraction of nonaromatics in the feed mixture.

In the 1960s, the German engineering company Krupp Koppers used *N*-formylmorpholine (NFM) to develop two processes. In the first, morphylex is used to recover all BTX aromatics from a feedstock low in aromatics

Table 6. **Composition of Typical Reformate, Vol %**

Component	Value
paraffins	20–30
cycloparaffins	2–3
aromatics	67–77
C_6	2–3
C_7	15–20
C_8	20–28
C_9	15–25
C_{10}	1–10

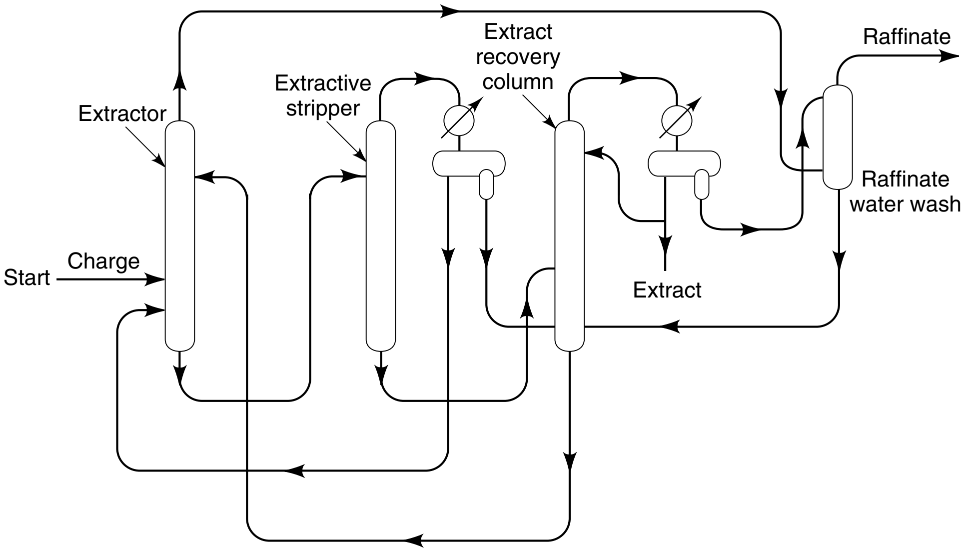


Fig. 4. Shell-UOP's Sulfolane extraction process (35). (Courtesy of Gulf Publishing Co.)

content. Morphylane, on the other hand, is an extractive distillation process used for the recovery of single aromatics, eg, toluene, benzene, from appropriate feedstocks. Octenar is a modified morphylane extractive distillation process used for recovering aromatics from catalytic reformates. Also in the 1960s, Union Carbide developed the Tetra process, using TTEG solvent (Fig. 5). In 1986, Union Carbide introduced the Carom process. Carom process

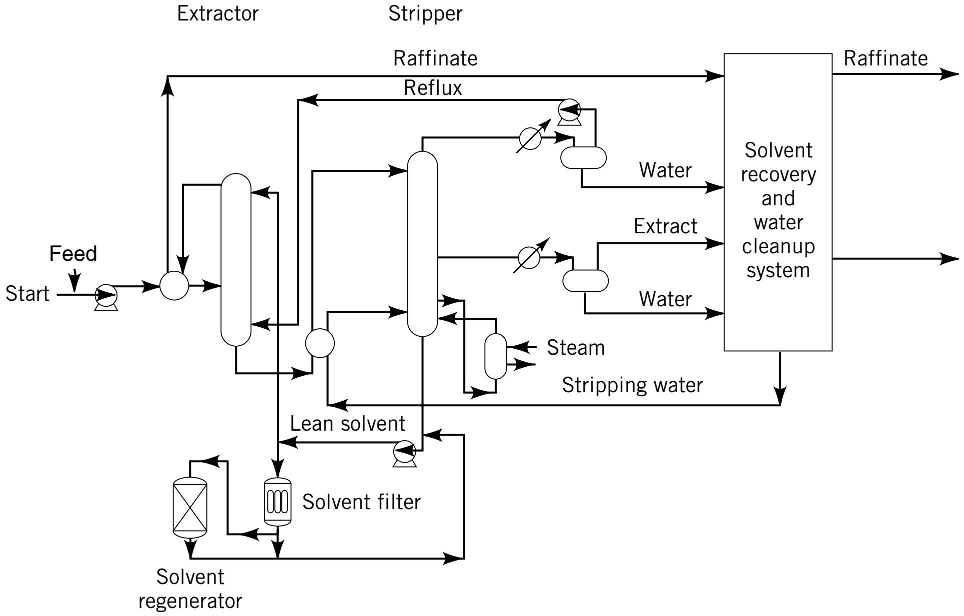


Fig. 5. Union Carbide Corp. Tetra extraction process (36). (Courtesy of Gulf Publishing Co.)

inherited design improvements over Udex and Tetra processes and uses TTEG combined with a proprietary cosolvent that enhances the capacity of the solvent system.

Sulfolane has a slight advantage over Carom in energy consumption, while Carom has 6–8% less capital for the same capacity Sulfolane unit. In 1995, Exxon (37) commercialized the most recent technology for aromatics recovery when it used copolymer hollow-fiber membrane in concentration-driven processes, pervaporation and perstraction, for aromatic–paraffin separation. Once the nonaromatic paraffins and cycloparaffins are removed, fractionation to separate the C_6 to C_9 aromatics is relatively simple.

Proper choice of feedstocks and use of relatively severe operating conditions in the reformers produce streams high enough in toluene to be directly usable for hydrodemethylation to benzene without the need for extraction.

Toluene is recovered from pyrolysis gasoline, usually by mixing the pyrolysis gasoline with reformate and processing the mixture in a typical aromatics extraction unit. Yields of pyrolysis gasoline and the toluene content depend on the feedstock to the steam-cracking unit, as shown in Table 7. Pyrolysis gasoline is hydrotreated to eliminate dienes and styrene before processing to recover aromatics.

4.2. Other Technologies for the Production of BTX from Light Hydrocarbons. Recent technological developments have centered on high temperature pyrolysis of light hydrocarbons C_2 to C_5, LPG, and naphtha to form aromatics in higher yields. Conversions were traditionally low because they were accompanied by a high degree of degradation to carbon and hydrogen. Recent improvements include modification of the thermal cracking process to produce higher yields of liquid products rich in aromatics and the extension of the catalytic hydroforming process to promote oligomerization and dehydrocyclization of the lower olefins. The common core of these developments is the use of shape-selective zeolite catalysts to promote the various reactions. One example is the commercialization of the Alpha process by Asahi Chemical Industry Company in Tokyo, an affiliate of Sanyo Petrochemical Company. The Alpha process uses modified ZSM-5 type zeolite catalyst to convert C_3–C_8 olefins at 490°C to aromatics at 510°C and $5\,\mathrm{kg/cm^2}$ pressure (see MOLECULAR SIEVES). Selectivity for toluene and xylenes peaks at 550°C but continues with increasing temperature for benzene. The Cyclar process (Fig. 6) developed jointly by BP and UOP uses a spherical, proprietary zeolite catalyst with a nonnoble metallic promoter to convert C_3 or C_4 paraffins to aromatics. The drawback to the process economics is the production of fuel gas, a low value by-product.

Table 7. **Toluene Content of Pyrolysis Gasoline, C_5 to 200°C**

Feedstock	Wt% to pyrolysis gasoline	Wt% toluene in pyrolysis gasoline
C_2–C_4 paraffin	5–10	7–15
naphthas	15–21	11–22
gas oils	17–20	13–19

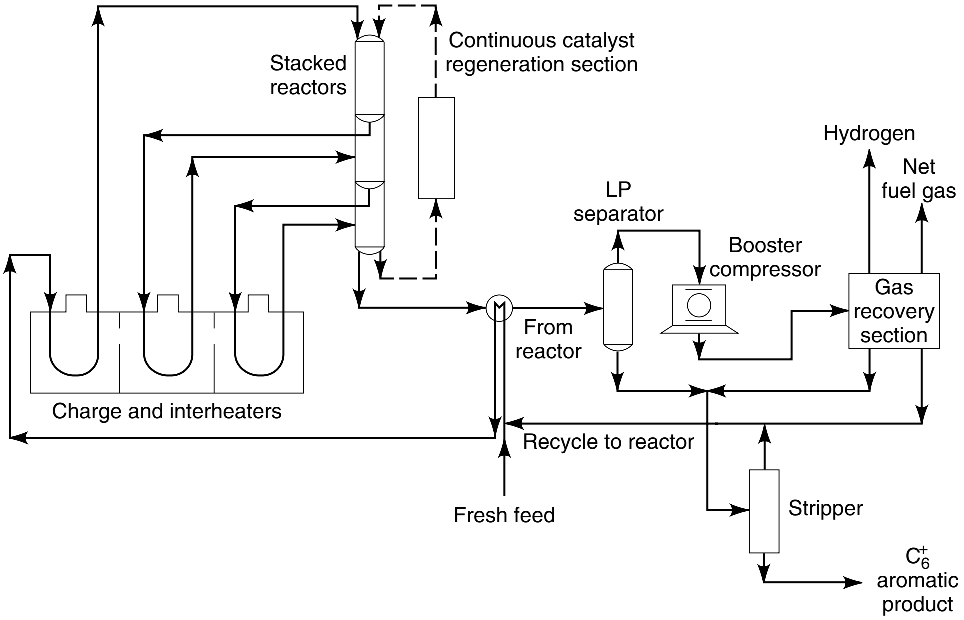


Fig. 6. UOP-BP Cyclar process for LPG aromatization (38). (Courtesy of Chem Systems Inc.)

BP operated a 1000-bpd demonstration unit in 1989–1991 in its refinery at Grangemouth, Scotland. UOP has agreement with Saudi Basic Industries Corporation (SABIC) to use Cyclar process in an aromatics plant at Yanbu, Saudi Arabia. Mitsubishi Oil and Chiyoda's Z-forming process (Fig. 7), which has been proven in a demonstration unit, shut down in December 1991 at Mitsubishi Oil's Kawasaki refinery, uses a metallosilicate zeolite catalyst to promote dehydrogenation of paraffins, followed by oligomerization and dehydrocyclization reactions. Feedstock consists of light naphtha or LPG. The BTX component of the product is mostly toluene.

ExxonMobil has a process (Fig. 8) that uses ZSM-5 zeolite catalyst with palladium and zinc promoters to oligomerize C_2 or C_3 to cyclohexane, which in turn is dehydrogenated to toluene, benzene, and xylenes. Similarly to this process, the KTI's Pyroform process (Fig. 9) uses a shape-selective zeolite catalyst to convert C_2 and C_3 paraffins to aromatics. The unique feature of this process is the design of proprietary reactor furnace and the operating temperature and pressure profiles. IF and Salute are developing the Aroformer process (Fig. 10) to use C_3–C_5, LPG, and light naphtha feedstocks. Chevron's Aromax process (Fig. 11) is similar to conventional catalytic reforming process, except that its feedstock has high paraffinicity and it has extra sulfur-removal facilities to avoid deactivating its L-type zeolite catalyst, which is very sensitive to sulfur.

Table 8 summarizes the Chem Systems' analysis of the cost of production of BTX from these feeds, resulting in a recommendation of the best-suited technology for each feedstock.

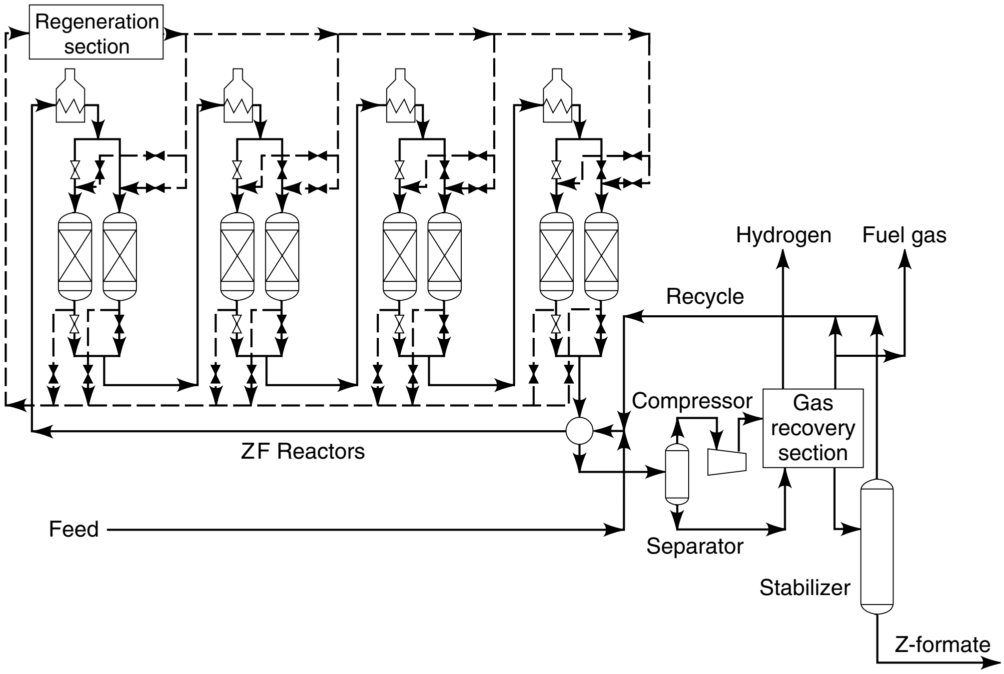


Fig. 7. Z-Forming process flow diagram (38). (Courtesy of Chem Systems Inc.)

5. Economic Aspects

The majority of toluene produced is unrecovered, ie, it remains in the various refinery streams. The largest concentrations of toluene are recovered from catalytic reformate and pyrolysis gasoline.

Recovered toluene demand in 2002 was 1.568 billion gallons, demand expected in 2006 is 1.710 billion gallons. Demand equals production plus imports minus exports. In 2002, 12 million gallons were exported and 87 million gallons were imported. U.S. demand is expected to grow at the rate of 1.5% through 2007 (39).

Table 9 gives U.S. producers of recovered toluene and their capacities. Toluene is recovered from catalytically reformed refinery streams (94%), pyrolysis gasoline derived from steam cracking to produce ethylene and propylene (5%), and as a by-product of styrene manufacture (1%) (40).

Demand in Western Europe decreased to 699 million gallons in 2002. Demand is lower than that in the United States because toluene disproportionation is not implemented as much and use of toluene as a solvent has declined. The five-year projection for demand is at −0.7% (39).

Japan's demand decreased also in 2002 to 453 million gallons. Demand in 2007 is expected to increase to 520 million gallons to support the production of benzene and xylene. Demand as a solvent will remain flat (39).

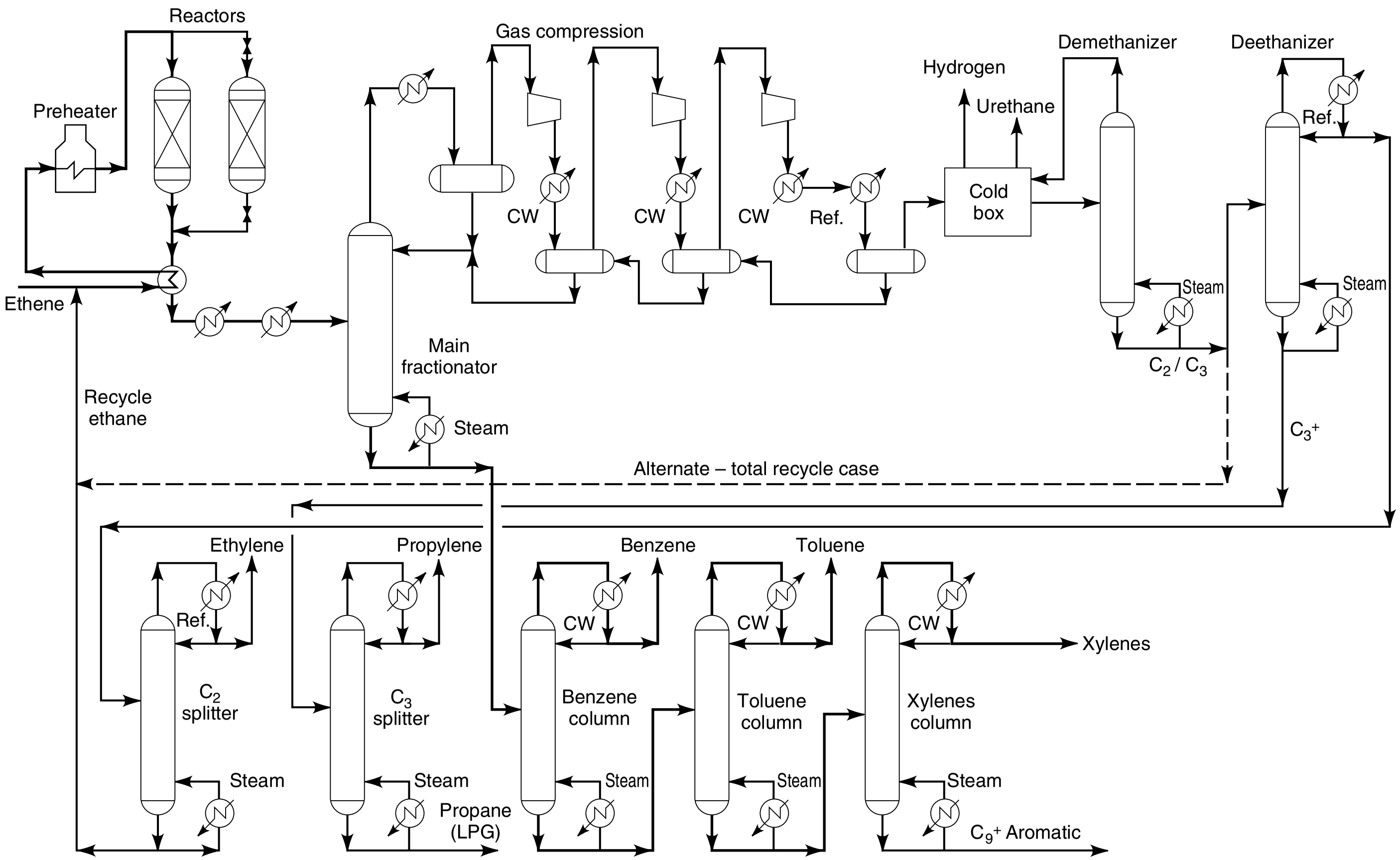


Fig. 8. ExxonMobil's process for aromatics from ethane (38). Ref. = refrigeration; CW = cooling water; Stm. = steam. (Courtesy of Chem Systems Inc.)

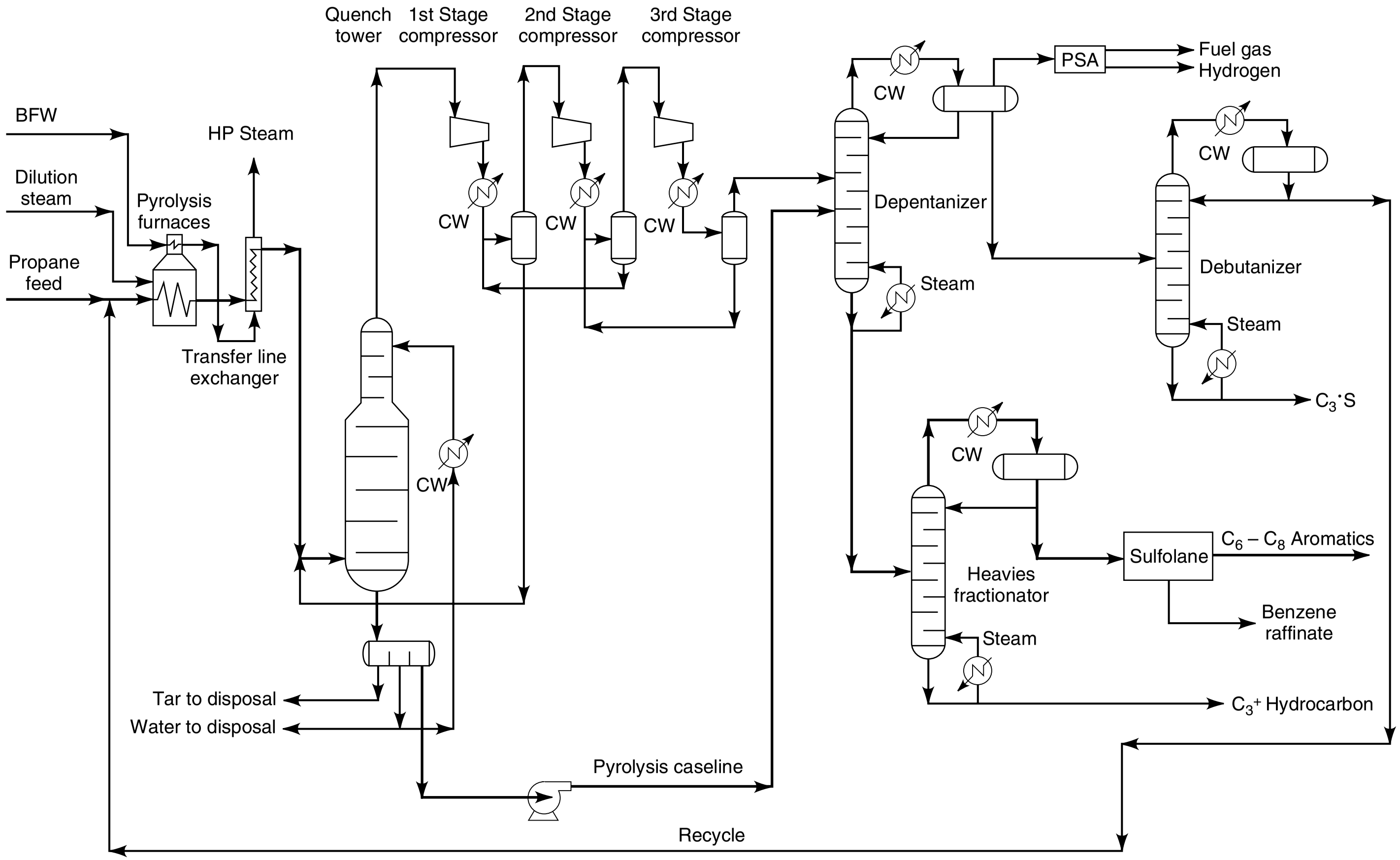


Fig. 9. Pyroform process flow diagram (38). Ref. = refrigeration, CW = cooling water, and BFW = boiling feed water. (Courtesy of Chem Systems Inc.)

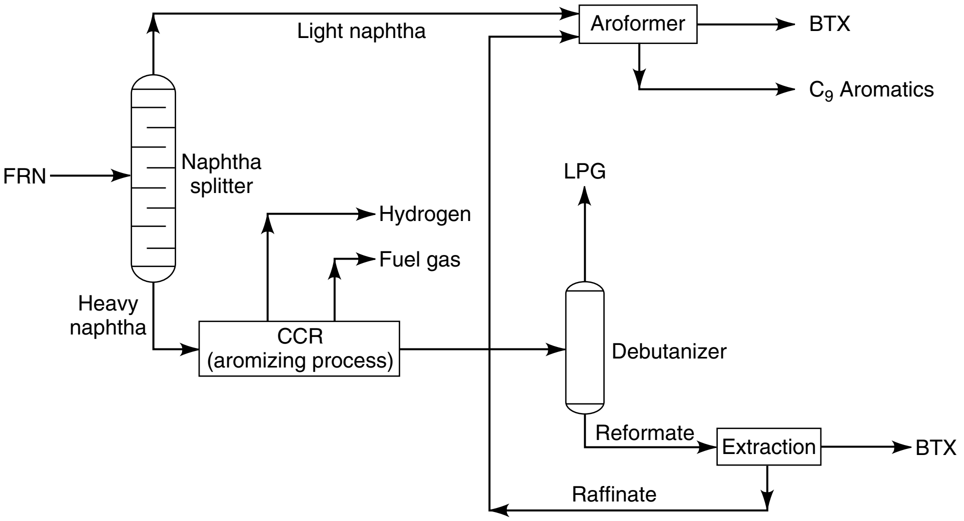


Fig. 10. Aromizing-Aroformer process overall flow plan (38). (Courtesy of Chem Systems Inc.)

In general, benzene/xylene production is the primary growth market because of the increasing demand for *p*-xylene. Toluene as a solvent will decline because of health and environmental regulations.

6. Specifications, Standards, and Quality Control

Toluene is marketed mostly as nitration and industrial grades. The generally accepted quality standards for the grades are given by ASTM D841 and D362, respectively, which are summarized in Tables 10 and 11, with the appropriate ASTM test method specified for determining the specification properties (41). Although the actual concentration of toluene in samples is not stipulated by these specifications, the purity is in fact controlled by the specific gravity and the boiling-range requirements of the method.

Purity of toluene samples as well as the number, concentration, and identity of other components can be readily determined using standard gas chromatography techniques (40–43). Toluene content of high purity samples can also be accurately measured by freezing point, as outlined in ASTM D1016. Toluene exhibits characteristic uv, ir, nmr, and mass spectra, which are useful in many specific control and analytical problems (2,44–46).

7. Analytical and Test Methods, Handling, Storage

Tables 10 and 11 list the analytical test methods for different properties of interest. The Manufacturing Chemists' Association, Inc. (MCA) has published the Chemical Safety Data Sheet SD 63, which describes in detail procedures for

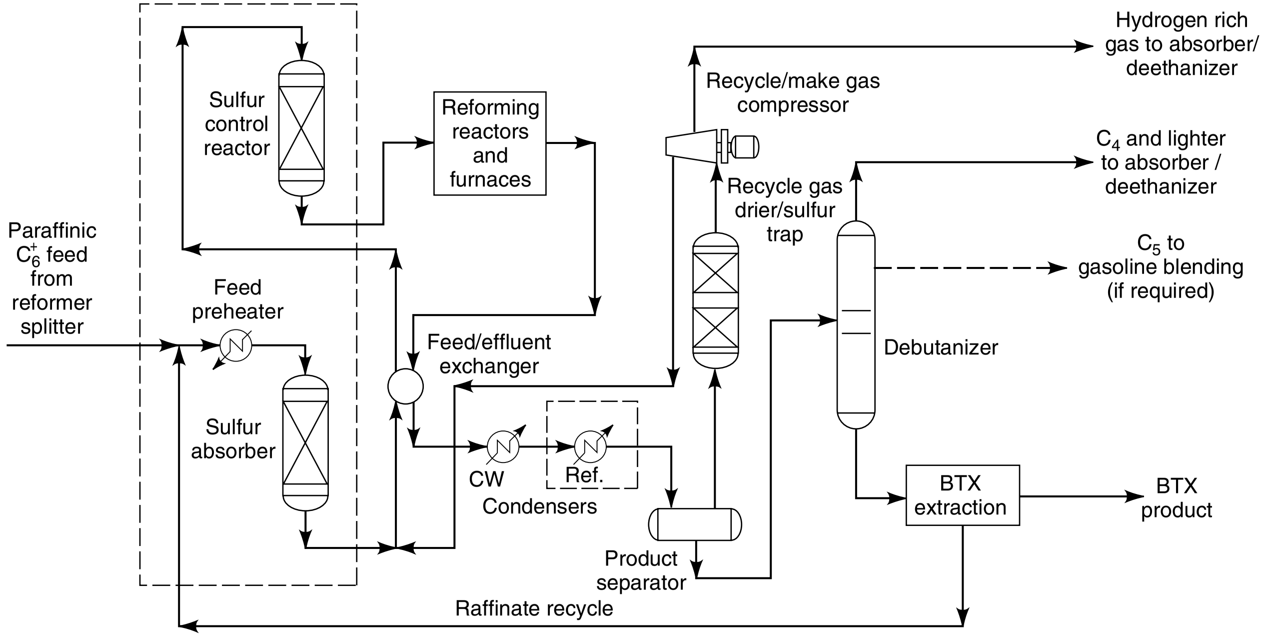


Fig. 11. Chevron's Aromax process for paraffins to BTX (38). (Courtesy of Chem Systems Inc.)

Table 8. **Best-Suited Developing Technology for Various Low Hydrocarbon Feedstocks**

Feedstock	Best-suited technology
C_2 paraffin (ethane)	ExxonMobil technology
C_3 paraffin (propane)	KTI's technology (Pyroform process)
C_4 paraffin (butane)	Mitsubishi's Z-Forming process
LPG	BP/UOP's Cyclar technology
light naphtha	Chevron's Aromax

safe handling of use of toluene (47). The Interstate Commerce Commission classifies toluene as a flammable liquid. Accordingly, it must be packaged in authorized containers, and shipping must comply with ICC regulations. Properties related to safe handling are autoignition temperature, 536°C; explosive limits, 1.27−7.0 vol% in air; and flash point 4.4°C, closed cup.

Table 9. **U.S. Producers of Toluene and Their Capacities**[a]

Producer	Location	Capacity, × 10^6gal
Atofina Petrochemicals	Port Arthur, Tex.	50
BP Chemicals	Texas City, Tex.	245
Chalmette Refining	Chalmette, La.	110
Citgo	Corpus Christi, Tex.; Lemont, Ill.	55
Clark Refining and Marketing	Lima, Ohio	105
Chevron Phillips Chemical	Port Arthur, Tex.	45
Chevron Phillips Chemical	Sweeny, Tex.; Guayama, P.R.	120
Dow Chemical	Plaquemine, La.	15
El Paso Energy	Corpus Christi, Tex.; Westvllie, N.J.	65
Equistar Chemicals	Alvin, Tex.; Channelview, Tex.; Corpus Christi, Tex.	70
ExxonMobil	Baton Rouge, La.; Baytown, Tex.; Beaumont, Tex.	275
Flint Hills Resources	Corpus Christi, Tex.	160
Frontier El Dorado Refining	El Dorado, Kan.	10
Hovensa	St. Croix, V.I.	900
Lyondell-Citgo Refining	Houston	35
Marathon Ashland Petroleum	Catlettsburg, Ky.; Texas City, Tex.	60
Shell Chemical	Deer Park, Tex.	35
Sunoco	Marcus Hook, Pa.; Philadelphia; Toledo, Ohio	145
Tosco	Alliance, La.	65
Valero Energy	Three Rivers, Tex.	45
by-product toluene from styrene production	Six sites	50
Total		*2,660*

[a] Ref. 40.

Table 10. **Specifications for Nitration-Grade Toluene, ASTM D841-80**[a]

Property	Specification	ASTM test method
sp gr, 20°/20°C	0.8690–0.8730	D891
color	no darker than 20 (max) on Pt–Co scale	D1209
distillation range at 101.3 kPa	no more than 1°C including 110.6°C for any one sample	D850
paraffins	no more than 1.5 wt %	D851
acid-wash color	no darker than no. 2 color standard	D848
acidity	no free acid, no evidence of acidity	D847
sulfur compound	free of H_sS and SO_2	D853
copper corrosion	copper strip shows no iridescence, gray or black deposit, or discoloration	D849

[a] Ref. 41.

Table 11. **Specifications for Industrial-Grade Toluene, ASTM D362-80**[a]

Property	Specification	ASTM test method
sp gr, 20°/20°C	0.860–0.874	D891
color	no darker than 20 (max) on Pt–Co scale	D1209
distillation range at 101.3 kPa	no more than 2°C from initial boiling point to dry point, including 110.6°C	D850, D1078
odor	characteristic aromatic hydrocarbon odor as agreed on by buyer and seller	D1296
water	insufficient to show turbidity at 20°C	
acidity	no more than 0.005 wt % (free acid calculated as acetic acid) equivalent to 0.047 mg KOH (0.033 mg NaOH) per g of sample or no free acid; that is, no evidence of acidity	D847
acid-wash color	no darker than no. 4 color standard	D848
sulfur compounds	free of H_2 and SO_2	D853
corrosion 1/2 h at 100°C	copper strip shows no greater discoloration than Class 2 in Method D1616	D1616
solvent power	100 min kauri–butanol value	D1113

[a] Ref. 41.

8. Health and Safety Factors

Permissible exposure limits established by the U.S. Department of Health and Human Services and the U.S. Department of Labor are summarized below, with the more restrictive levels proposed by NIOSH (48).

	OSHA, mg/m^3 (ppm)	NIOSH, mg/m^3 (ppm)
average during 8-h shift (TWA)	752 (200)	376 (100)
not to exceed	1129 (300)	
except for 10-min average (TLV)	1181 (500)	752 (200)

Table 12. **Physiological Response to Inhaled Toluene**[a]

Level, mg/L (ppm)	Result
0.38 (100)	transient irritation, psychological effects
0.76 (200)	transitory mild upper respiratory-tract irritation
1.52 (400)	mild eye irritations, lacrimation, hilarity
2.28 (600)	lassitude, hilarity, slight nausea
3.03 (800)	rapid irritation, nasal secretion, metallic taste, drowsiness, and impaired balance

[a] Ref. 49.

Toluene generally resembles benzene closely in its toxicological properties; however, it is devoid of benzene's chronic negative effects on blood formation (49). General effects of inhalation are summarized in Table 12. A detailed discussion of physiological response may be found in Reference 49. The odor threshold for toluene has been determined to be ca 9.5 mg/m^3 (2.5 ppm) (50). In the human system, toluene is oxidized to benzoic acid, which in turn reacts with glycine to form hippuric acid, *N*-benzoylglycine, which is excreted in the urine. However, in animals the development of inflammatory and ulcerous lesions of the penis, prepuce, and scrotum have been demonstrated after inhalation of toluene. This implies that the metabolic processing of toluene produces irritating metabolites.

9. Uses

It is difficult to estimate the total actual production capacity for toluene because it is dependent on the feedstocks used, the number of units operated, and the operating conditions of the units. About 85–90% of toluene produced annually in the United States is not isolated but is blended directly into the gasoline pool as a component of reformate and of pyrolysis gasoline. Capacity exists to isolate ca 2.7×10^9 gal per year, of which about 75–80% is used for chemicals and solvents or exported. The remainder is blended into gasoline to increase octane number of premium fuels. The largest use of toluene for chemicals (ca 50% in 2002) is in hydrodealkylation (HDA) operations to produce benzene. Remaining chemical uses are production of xylene (20%), solvents (12%), Toluene diisocyanate (8%), and miscellaneous uses (10%). Miscellaneous includes benzoic acid, benzyl chloride, benzaldehydes and toluene sulfonic acid.

9.1. Automotive Fuels. About 90% of the toluene generated by catalytic reforming is blended into gasoline as a component of $> C_5$ reformate. The octane number ($R + M/2$) of such reformates is typically in the range of 88.9–94.5, depending on severity of the reforming operation. Toluene itself has a blending octane number of 103–106, which, as shown in Table 13, is exceeded only by oxygenated compounds such as methyl *tert*-butyl ether, ethanol, and methanol.

Toluene is, therefore, a valuable blending component, particularly in unleaded premium gasolines. Although reformates are not extracted solely for the purpose of generating a high octane blending stock, the toluene that is coproduced when xylenes and benzene are extracted for use in chemicals, and that exceeds demands for use in chemicals, has a ready market as a blending component for gasoline.

Table 13. **Blending Octane Number, $(R+M)/2^a$, for Selected Components in Unleaded Gasoline**

Component	$(R+M)/2$	References
methanol	120, 117	(46,47)
ethanol	119, 113, 117	(46–48)
methyl *tert*-butyl ether	108, 106, 111	(46–48)
tert-butyl alcohol	97.5, 94.5, 96	(46–48)
toluene	106, 103.5, 102.9	(47–49)
C_8 aromatics	105.5	49
unleaded regular	88.0	50
unleaded premium	93.0	50

[a] R = Research method octane rating, ASTM D2699; M = motor method octaine rating, ASTM D2700.

As a blending component in automotive fuels, toluene has several advantages. First, as shown in Table 13, it has a high octane number compared to regular and premium unleaded gasoline. Second, its relatively low volatility permits incorporation into gasoline blends of other available and less expensive materials, eg, *n*-butane, with relatively high volatility. Since the principal use of toluene is in gasoline, with only a small amount used in chemicals, there will always be an available supply for chemicals manufacture at a price essentially fixed by the value of toluene as a blending component in gasoline.

9.2. Manufacture of Benzene. Toluene is converted to benzene by hydrodemethylation either under thermal or catalytic conditions. Benzene produced from this source generally supplies 25–30% of the total benzene demand. Reaction conditions generally range from 600–800°C at 3.55–7.00 MPa (500–1000 psi), and the reaction is exothermic. Conversion per pass is 60–90% with selectivities to benzene $>95\%$. With catalysts, typically supported Cr_2O_3, Mo_2O_3, and CoO, operating temperatures are lower than in the thermal process and selectivities are higher. These gains, however, are offset by the need to decoke the catalyst periodically. Losses to by-product formation, particularly biphenyls, are controlled by recycle of these materials to the reaction zone (51,52). A flow scheme for a typical catalytic process (52) is shown in Figure 12.

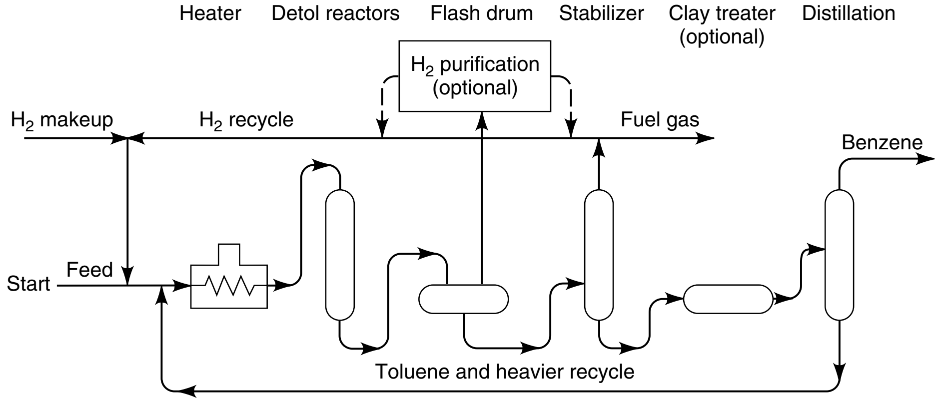


Fig. 12. Air Products and Chemicals toluene dealkylation (Detol) process (52). (Courtesy of Gulf Publishing Co.)

The feedstock is usually extracted toluene, but some reformers are operated under sufficiently severe conditions or with selected feedstocks to provide toluene pure enough to be fed directly to the dealkylation unit without extraction. In addition to toluene, xylenes can also be fed to a dealkylation unit to produce benzene.

9.3. Use as Solvent.

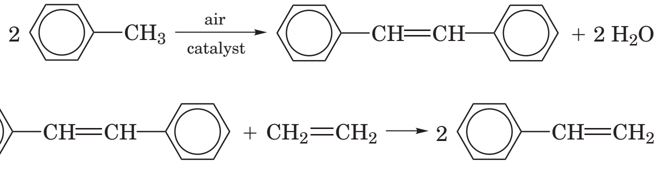
Toluene is more important as a solvent than either benzene or xylene. Solvent use accounts for ca 12% of the total U.S. toluene demand for chemicals. About two-thirds of the solvent use is in paints and coatings; the remainder is in adhesives, inks, pharmaceuticals, and other formulated products utilizing a solvent carrier. Use of toluene as solvent in surface coatings has been declining, primarily because of various environmental and health regulations. It is being replaced by other solvents, such as esters and ketones, and by changing the product formulation to use either fully solid systems or water-based emulsion systems.

9.4. Styrene from Toluene.

Processes for forming styrene by reaction of methanol with toluene have been reported in both the Japanese and former USSR literature, and in the United States a patent has been issued to Monsanto (54–57). In the latter case, an X-type faujasite aluminosilicate, exchanged with cesium and promoted with either boron or phosphorus, was used as the catalyst. Toluene and methanol at a 5:1 mol ratio react at 400−475°C. About half the methanol is converted to an ethylbenzene−styrene mixture and about half is converted to carbon monoxide and hydrogen. Yields of toluene are very high. Provision must still be made for dehydrogenation of the ethylbenzene in the mixture. The product stream is quite dilute, ca 5%, necessitating large recycles. Because of the generation of carbon monoxide and hydrogen, such a plant would need to operate in conjunction with a methanol synthesis plant, a significant process disadvantage which may possibly be overcome by catalyst development.

Chem Systems Inc. proposed a process in which benzyl alcohol obtained by an undisclosed direct oxidation of toluene is homologated with synthesis gas to yield 2-phenylethyl alcohol, which is then readily dehydrated to styrene (58). This process eliminates the intermediate formation of methanol from synthesis gas but does require the independent production of benzyl alcohol.

A different approach, taken by both Monsanto (59) and Gulf Research and Development Company (60), involved the oxidative coupling of two molecules of toluene to yield stilbene. The stilbene is then subjected to a metathesis reaction with ethylene to yield two molecules of styrene.



A significant problem is the dehydrocoupling reaction, which proceeds only at low yields per pass and is accompanied by rapid deactivation of the catalyst. The metathesis step, although chemically feasible, requires that polar contaminants resulting from partial oxidation be removed so that they will not deactivate the metathesis catalyst. In addition, apparently both *cis*- and *trans*-stilbenes are obtained; consequently, a means of converting the unreactive *cis*-stilbene to the more reactive trans isomer must also be provided, thus complicating the process.

9.5. Potential Uses.

para-Methylstyrene. Mobil Chemical has a process for the manufacture of *para*-methylstyrene from toluene (61,62). This monomer is produced by alkylating toluene with ethylene, using the Mobil ZSM-5 zeolite catalyst. The alkylation is highly selective, reportedly producing the para isomer with 97% selectivity. Conventional technology, employing a special catalyst to minimize by-products and optimize conversion, is used to dehydrogenate the *para*-ethyltoluene to *para*-methylstyrene.

Vinyltoluene, comprising a mixture of ca 33% *para*- and 67% *meta*-methylstyrene, has been marketed for ca 45 yr by Dow Chemical Company and also by Cosden. However, the performance properties of the polymers prepared from the para isomer are not only superior to those of the polymer prepared from the typical mixed isomers, but are generally superior to those of polystyrene (61). This advantage, coupled with a raw material cost advantage over styrene, suggests that *para*-methylstyrene may displace significant amounts of styrene.

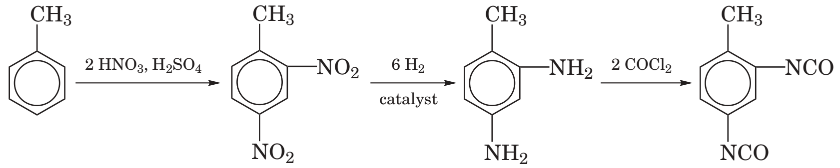
Terephthalic Acid from Toluene. Both carbon monoxide and methanol can react with toluene to yield intermediates that can be oxidized to terephthalic acid. In work conducted mainly by Mitsubishi Gas Chemical Company (63,64), toluene reacts with carbon monoxide and molar excesses of HF and BF_3 to yield a *para*-tolualdehyde–HF–BF_3 complex. Decomposition of this complex under carefully controlled conditions recovers HF and BF_3 for recycle and *para*-tolualdehyde, which can be oxidized in place of *para*-xylene to yield terephthalic acid. One drawback of the process is the energy-intensive, and therefore high cost, decomplexing step. The need for corrosion-resistant materials for construction and the need for extra design features to handle the relatively hazardous HF and BF_3 also add to the cost. This process can be advantageous where toluene is available and xylenes are in short supply.

A second approach is the selective alkylation of toluene with methanol to yield C_8 aromatic mixtures containing 70–90% *para*-xylene and generally $< 1\%$ of ethylbenzene (65). Such C_8 aromatic mixtures are excellent feedstocks for recovery of high purity *para*-xylene. The high selectivity to *para*-xylene is achieved by modifying typical HZMS-5 silica aluminate zeolites (66) with phosphorus and boron. This process is not used commercially, probably because current feedstock needs for manufacture of terephthalic acid are met by *para*-xylene from typical reformate, and because conversions of toluene in the process are relatively low (ca 20% per pass) and significant amounts of methanol are converted to by-products such as HCHO, CO, CO_2, CH_4, C_2H_4, and C_3H_6 where stoichiometric quantities of methanol are used. Best results are obtained at 4:1 and higher mole ratios of toluene to methanol. Improved selectivity of the catalyst to permit better utilization of the methanol would enhance the economics of this process.

10. Derivatives

10.1. Toluene Diisocyanate.

Toluene diisocyanate (TDI) is the basic raw material for production of flexible polyurethane foams. It is produced by the reaction sequence shown below, in which toluene is dinitrated, the dinitrotoluene is hydrogenated to yield 2,4-diaminotoluene, and this diamine in turn is treated with phosgene to yield toluene 2,4-diisocyanate.

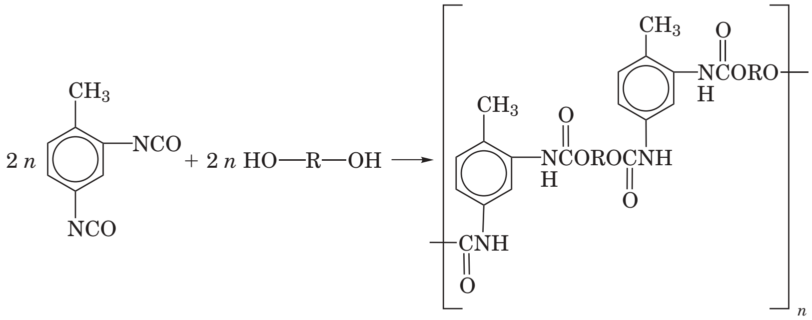


The nitration step produces two isomers, 2,4-dinitrotoluene and 2,6-dinitrotoluene, the former predominating. Mixtures of the two isomers are frequently used, but if single isomers are desired, particularly the 2,4-dinitrotoluene, nitration is stopped at the mono stage and pure *para*-nitrotoluene is obtained by crystallization. Subsequent nitration of this material yields only 2,4-dinitrotoluene for conversion to the diisocyanate.

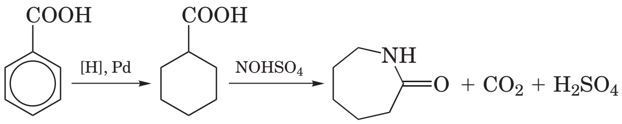
Polyurethane foams are formed by reaction with glycerol; with poly(propylene oxide), sometimes capped with poly(ethylene oxide) groups; with a reaction product of trimethylolpropane and propylene oxide; or with other appropriate polyols. A typical reaction sequence is shown below, in which HO–R–OH represents the diol. If a triol is used, a cross-linked product is obtained.

Water, in small amount, reacts with the diisocyanate to generate carbon dioxide, and amine and is used most frequently as the foaming agent.

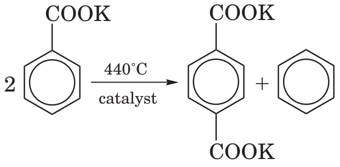
Flexible polyurethane foams constitute the largest market for TDI. Adhesives and sealants is another sector of the TDI market. Consumption of TDI in the U.S. in 2004 increased 9% over the use in 2003 (67).



10.2. Benzoic Acid. Benzoic acid is manufactured from toluene by oxidation in the liquid phase using air and a cobalt catalyst. Typical conditions are 308–790 kPa (30–100 psi) and 130–160°C. The crude product is purified by distillation, crystallization, or both. Yields are generally >90 mol%, and product purity is generally $>99\%$. Noveon Kalama, the largest producer, converts about half of its production to phenol, but most producers consider the most economic process for phenol to be peroxidation of cumene. Other uses of benzoic acid are for the manufacture of benzoyl chloride, of plasticizers such as butyl benzoate, and of sodium benzoate for use in preservatives. In the U.S., 49% of benzoic acid use is in the production of benzoate plasticizers (68). In Italy, Snia Viscosa uses benzoic acid as raw material for the production of caprolactam, and subsequently nylon-6, by the sequence shown below.

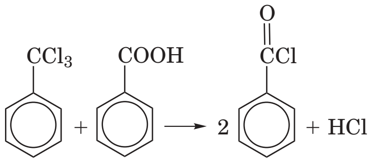


The Henkel process employing potassium benzoate has been used in Japan for the manufacture of terephthalic acid by the following scheme:



The Henkel process provides a means to convert toluene to benzene and at the same time makes use of the methyl group. Neither of these two processes is economically attractive for use in the United States.

10.3. Benzyl Chloride. Benzyl chloride is manufactured by high temperature free-radical chlorination of toluene. The yield of benzyl chloride is maximized by use of excess toluene in the feed. More than half of the benzyl chloride produced is converted by butyl benzyl phthalate by reaction with monosodium butyl phthalate. The remainder is hydrolyzed to benzyl alcohol, which is converted to aliphatic esters for use in soaps, perfume, and flavors. Benzyl salicylate is used as a sunscreen in lotions and creams. By-product benzal chloride can be converted to benzaldehyde, which is also produced directly by oxidation of toluene and as a by-product during formation of benzoic acid. By-product benzotrichloride is not hydrolyzed to make benzoic acid but is allowed to react with benzoic acid to yield benzoyl chloride.



10.4. Disproportionation to Benzene and Xylenes. With acidic catalysts, toluene can transfer a methyl group to a second molecule of toluene to yield one molecule of benzene and one molecule of mixed isomers of xylene.

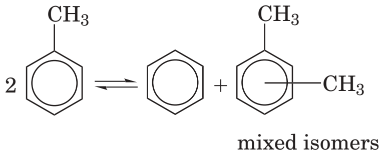


Table 14. **Equilibrium Distribution for Toluene Disproportionation[a], Mol %**

Temperature, K	Benzene	Toluene	Xylenes
300	31.3	37.4	31.3
400	28.8	42.4	28.8
500	26.5	47.0	26.5
600	23.9	52.2	23.9
700	21.4	57.2	21.4
800	18.7	62.6	18.7
900	16.2	67.6	16.2
1000	13.6	72.8	13.6

[a] Ref. 69.

This disproportionation is an equilibrium reaction for which typical distributions are shown in Table 14. Disproportionation generates benzene from toluene and at the same time takes full advantage of the methyl group to generate a valuable product, ie, xylene. Economic utility of the process is strongly dependent on the relative values of toluene, benzene, and the xylenes. This xylene, which contains little or no ethylbenzene, at one time would have commanded a premium as a feed for *para*-xylene units. However, ethylbenzene-free feeds offer little advantage because the zeolite-based isomerization catalysts, eg, the Mobil ZSM-5 and the Amoco AMS-1B molecular sieves, very selectively hydrodeethylate and disproportionate ethylbenzene as they isomerize xylenes. Accordingly, toluene disproportionation processes have little advantage over catalytic reforming for production of xylenes. Operation of plants can be justified only where there is an excess of toluene and where both xylenes and benzene are a desired product. The disproportionation plant can then replace a toluene demethylation unit. By proper selection of catalysts, the xylene production can be controlled to give high selectivity to the para isomer; however, in order to accomplish this, catalyst reactivity is greatly diminished (70).

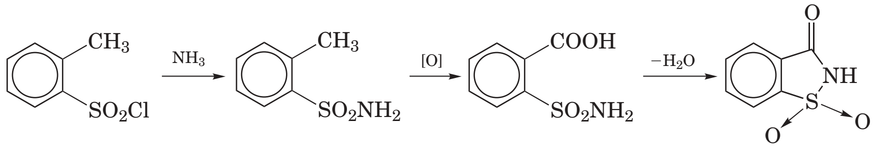
10.5. Vinyltoluene. Vinyltoluene is produced by Dow Chemical Company and is used as a resin modifier in unsaturated polyester resins. Its manufacture is similar to that of styrene; toluene is alkylated with ethylene, and the resulting ethyltoluene is dehydrogenated to yield vinyltoluene.

10.6. Toluenesulfonic Acid. Toluene reacts readily with fuming sulfuric acid to yield toluene–sulfonic acid. By proper control of conditions, *para*-toluenesulfonic acid is obtained. The primary use is for conversion, by fusion with NaOH, to *para*-cresol. The resulting high purity *para*-cresol is then alkylated with isobutylene to produce 2,6-di-*tert*-butyl-*para*-cresol (BHT), which is used as an antioxidant in foods, gasoline, and rubber. Mixed cresols can be obtained by alkylation of phenol and by isolation from certain petroleum and coal–tar process streams.

The toluenesulfonic acid prepared as an intermediate in the preparation of *para*-cresol also has a modest use as a catalyst for various esterifications and condensations. Sodium salts of the toluenesulfonic acids are also used in surfactant formulations.

10.7. Benzaldehyde. Benzaldehyde is produced mainly as by-product during oxidation of toluene to benzoic acid, but some is produced by hydrolysis of benzal chloride. The main use of benzaldehyde is as a chemical intermediate for production of fine chemicals used for food flavoring, pharmaceuticals, herbicides, and dyestuffs.

10.8. Toluenesulfonyl Chloride. Toluene reacts with chlorosulfonic acid to yield both *ortho*- and *para*-toluenesulfonyl chlorides. The ortho isomer is converted to saccharin.



The para isomer is used for preparation of specialty chemicals.

BIBLIOGRAPHY

"Toluene" in *ECT* 1st ed., Vol. 14, pp. 262–273, by M. Lapeyrouse, Esso Research and Engineering Co.; in *ECT* 2nd ed., Vol. 20, pp. 527–565, by H. E. Cier, Esso Research and Engineering Co.; in *ECT* 3rd ed., Vol. 23, pp. 246–273, by M. C. Hoff, Amoco Chemicals Corp.; in *ECT* 4th ed., Vol. 24, pp. 350–389, by E. Dickson Ozokwelu, Amoco Chemical Co.

CITED PUBLICATIONS

1. *Design Institute for Physical Properties Research*, Project 801, Data Compilation, 1995 *Beilstein Online*, Beilstein Institute for Organic Chemistry, Springer-Verlag, Heidelberg, Germany, 1995.
2. *American Petroleum Institute Research Project 44*, Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A&M University, College Station, Tex., 1976.
3. *Technical Data Book—Petroleum Refining*, 4th ed., Refining Department, American Petroleum Institute, 1983.
4. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill Book Co., Inc., New York, 1987.
5. D. T. Jamieson, J. B. Irving, and J. S. Tudhope, *Liquid Thermal Conductivity: A Data Survey to 1973*, National Engineering Laboratory, Edinburgh, Scotland, 1975.
6. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Robert E. Krieger Publishing Co., Malabar, Fla., 1987.
7. B. D. Smith and R. Srivastava, *Thermodynamic Data for Pure Compounds: Part A. Hydrocarbons and Ketones*, Elsevier, Amsterdam, the Netherlands, 1986.
8. T. Boublik, V. Fried, and E. Hala, *The Vapour Pressures of Pure Substances*, 2nd ed., Elsevier, Amsterdam, the Netherlands, 1984.
9. H. Knapp, R. Doring, L. Oellrich, U. Plocker, and J. M. Prausnitz, *Vapor–Liquid Equilibria for Mixtures of Low Boiling Substances*, Chemistry Data Series, Vol. VI, Dechema, 1982.
10. I. Wichterle, J. Linek, and E. Hala, *Vapor–Liquid Equilibrium Data Bibliography*, Elsevier Scientific Publishing Co., Amsterdam, the Netherlands, 1973, with Suppls. I, II, III, and IV, 1976, 1979, 1982, and 1985, respectively.

11. J. Wisniak and A. Tamir, *Liquid–Liquid Equilibrium and Extraction*, Elsevier Scientific Publishing Co., Amsterdam, Pt. A, 1980 Pt. B, 1981 Suppl. 1, 1985 Suppl. 2, 1987.
12. L. H. Horsley, *Azeotropic Data-III*, Advances in Chemistry Series, No. 116, American Chemical Society, Washington, D.C., 1973.
13. J. Gmehling, J. Menke, K. Fischer, and J. Krafczyk, *Azeotropic Data: Part II*, VCH Publishers, Inc., New York, 1994.
14. L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.* **71**, 3644 (1949) **72**, 3113 (1950).
15. H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.* **74**, 3570 (1952).
16. R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.* **80**, 2778 (1958).
17. D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.* **73**, 2013 (1951).
18. D. A. McCaulay and co-workers, *Ind. Eng. Chem.* **42**, 2103 (1950).
19. C. K. Ingold and co-workers, *J. Chem. Soc.*, 1959 (1931).
20. F. E. Condon, *J. Am. Chem. Soc.* **70**, 1963 (1948).
21. H. Pines and co-workers, *J. Chem. Soc.* **77**, 554 (1955).
22. G. G. Eberhardt and H. J. Peterson, *J. Org. Chem.* **30**, 82 (1965).
23. G. G. Eberhardt and W. A. Butte, *J. Org. Chem.* **29**, 2928 (1964).
24. H. Pines and L. A. Schaap in H. Pines and L. A. Schaap *Advances in Catalysis*, Vol. XII, Academic Press, New York, 1960, p. 117.
25. B. T. Brooks and co-workers, *The Chemistry of Petroleum Hydrocarbons*, Van Nostrand Reinhold Company, New York, 1955, “Chapt. 56”.
26. M. S. Kharasch and M. J. Berkman, *J. Org. Chem.* **6**, 810 (1941).
27. H. Pines, *The Chemistry of Catalysis Hydrocarbon Conversions*, Academic Press, Inc., New York, 1981, 173–174.
28. *Hydrocarbon Process.* **60** (11), 147 (1981).
29. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd ed., Allyn & Bacon, Inc., Boston, Mass., 1973, p. 323.
30. *Hydrocarbon Process.* **55** (5), 75 (May 1976).
31. R. Coates and co-workers, *Proc. API Div. Refin.* **53**, 251 (1973).
32. E. A. Sutton, A. R. Greenwood, and F. H. Adams, *Oil Gas J.* **70**(21), 52 (May 22, 1972).
33. Ref. 17, 101–110.
34. J. H. Gary and G. E. Handwark, *Petroleum Refining Technology and Economics*, Marcel Dekker, Inc., New York, 1975, 65–85.
35. J. E. Germain, *Catalytic Conversion of Hydrocarbons*, Academic Press, Inc., New York, 1969.
36. D. B. Broughton and G. F. Asselin, *Proc. Second World Pet. Congr.* **4**, 65 (1967).
37. R. C. Schucker, *AIChE National Meeting Topical Conference Preprints*, Vol. 1, 357–379, Miami Beach, Fla., Nov. 12–17, 1995.
38. *1995 PERP Report No. 93-7 on Benzene/Toluene*, Chem Systems Inc., Tarrytown, N.Y., 1995.
39. “Toluene”, *Chemical Economics Handbook*, SRI Consulting, Menlo Park, Calif., Nov. 2003.
40. “Toluene, Chemical Profile”, *Chem. Market Reporter*, 27 (May 5, 2003).
41. *1992 Annual Book of ASTM Standards*, Sect. 6, Vol. 06.03, American Society for Testing and Materials, Philadelphia, Pa., 1992.
42. C. L. Stucky, *J. Chromatogr. Sci.* **7**, 177 (1969).
43. H. M. McNaire and E. J. Bonelli, *Basic Gas Chromatography*, Varian Aerograph, Walnut Creek, Calif. R. R. Freeman, ed., *High Resolution Gas Chromatography*, 2nd ed., Hewlett-Packard Co., Palo Alto, Calif., 1981.

44. *The Sadtler Standard Spectra*, Sadtler Research Laboratories, Philadelphia, Pa., 1971.
45. C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, 2nd ed., Aldrich Chemical Co., 1975.
46. J. G. Grasselli, *Atlas of Spectral Data and Physical Constants for Organic Compounds*, CRC Press, Cleveland, Ohio, 1973.
47. *Chemical Safety Data Sheet SD-63, Toluene*, Manufacturing Chemists' Association, Washington, D.C., 1956.
48. U.S. Department of Health and Human Services, *Occupational Health Guidelines for Chemical Hazards*, DHHS (NIOSH) Pub. No. 81-123, U.S. Government Printing Office, Washington, D.C., Jan. 1981.
49. E. Bingham, B. Cohrssen, and C. Powell, eds., *Patty's Toxicology*, 5th ed., Vol. 4, John Wiley & Sons, Inc., New York, 2001, pp. 252–258.
50. C. P. Carpenter and co-workers, *Toxicol. Appl. Pharmacol.* **26**, 473 (1976).
51. K. Weissermel and H. Arpe, *Industrial Organic Chemistry*, Verlag Chemie, New York, 1978, 288–289.
52. *Hydrocarbon Process.* (11), 138 (Nov. 1981).
53. A. L. Waddams, *Chemicals from Petroleum*, 4th ed., John Murray, London, 1978, "Chapt. 13".
54. T. Yashima and co-workers, *J. Catal.* **26**, 303 (1972).
55. H. Itoh and co-workers, *J. Catal.* **64**, 284 (1980).
56. USSR Pat. 188,958 (Oct. 11, 1965), (to USSR).
57. U.S. Pat. 4,115,424 (Dec. 22, 1976), M. L. Unland and G. E. Barker (to Monsanto Co.).
58. A. P. Gelbein, *Toluene–Synthesis Gas Based Routes to Styrene, An Assessment*, ACS Petro Chemical Division, New York, Aug. 23–28, 1981.
59. U.S. Pat. 3,965,206 (Dec. 12, 1974), P. D. Montgomery, R. N. Moore, and W. R. Knox (to Monsanto Company).
60. R. A. Innes and H. E. Swift, *Chemtech*, 244 (Apr. 1981).
61. *Chem. Week*, 42 (Feb. 17, 1982).
62. *Chem. Eng. News*, 20 (May 31, 1982).
63. S. Fujiyama and T. Kashara, *Hydrocarbon Process.* **11**, 147 (1978).
64. A. Mitsutani, *Terephthalic Acid from Toluene*, R&D Review Report No. 8, Nippon Chemtec Consulting, Inc., Feb. 1978.
65. W. W. Kaeding and co-workers, *J. Catal.* **67**, 159 (1981).
66. U.S. Pat. 3,702,886 (Oct. 19, 1969), R. J. Arganer and R. G. Landolt (to Mobil Oil Co.).
67. "Toluene Diisocyanate, Chemical Profile", *Chem. Market Reporter*, 23 (Feb. 14, 2005).
68. "Benzoic acid, Chemical Profile", *Chem. Market Reporter*, 23 (March 21, 2005).
69. D. R. Stull and co-workers, *Chemical Thermodynamics of Hydrocarbon Compounds*, John Wiley & Sons, Inc., New York, 1969, p. 368.
70. W. W. Kaeding and co-workers, *J. Catal.* **69**, 392 (1981).

E. DICKSON OZOKWELU
Amoco Chemical Company