

## BTX PROCESSING

Benzene [71-43-2] (B), toluene [108-88-3] (T), and the xylenes (X) are the lowest molecular weight aromatic hydrocarbon homologues. They are each very large scale chemical feedstocks. Since they are often produced together in the same process, they can be considered as a group, ie, BTX. However, BTX as such is not an article of commerce. It is either an important component of a crude mixture such as reformat or pyrolysis gasoline, or it is separated and purified into its individual components. This article mainly discusses the processes for making those crude mixtures. Other articles cover the physical and chemical properties of the individual BTX compounds themselves (see Benzene; Toluene; and Xylenes and ethylbenzene). This article focuses on technology involving the group as a whole.

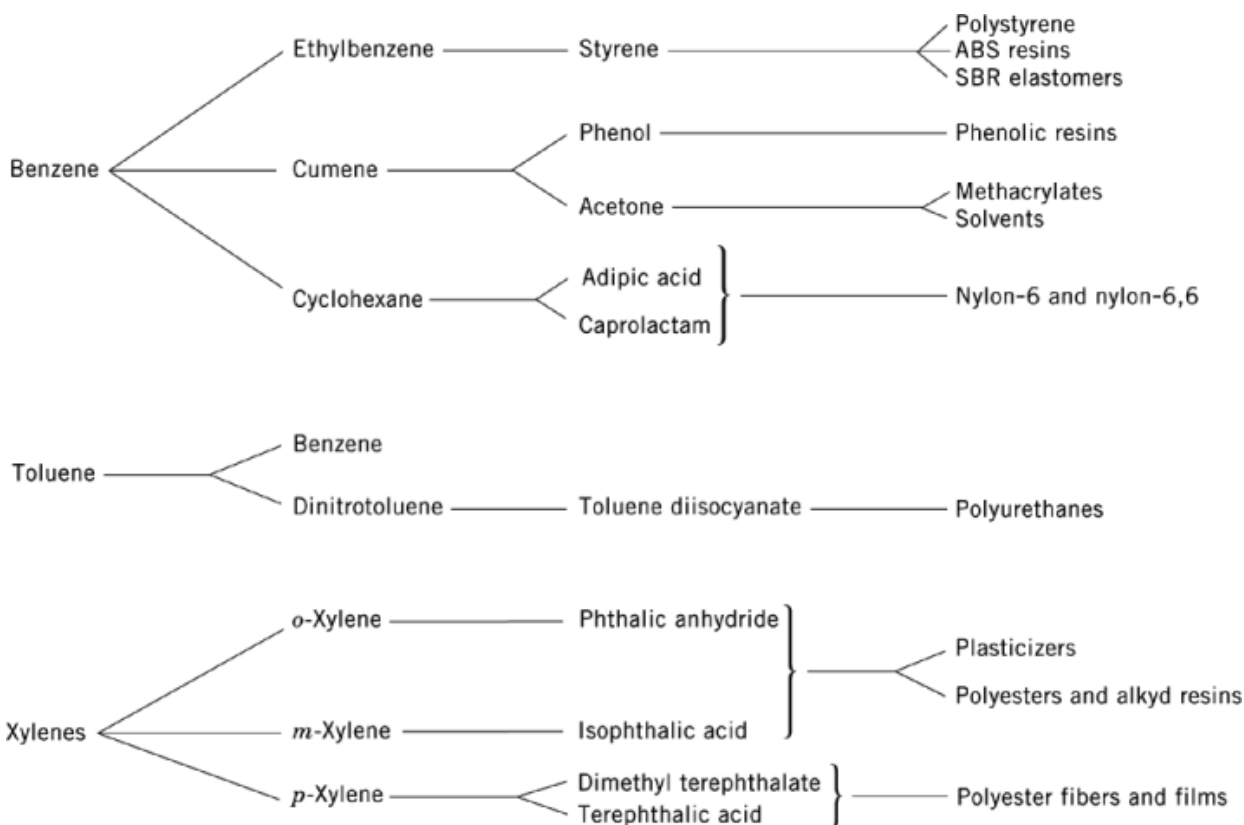
Originally BTX was obtained commercially by pyrolysis of coal (see Coal). Since World War II, the production of BTX has been intimately connected with the production of gasoline. BTX constitutes part of an important gasoline component called reformat which is discussed below (see Gasoline and other motor fuels). Reformat is highly valued for gasoline because it has a very high octane rating. This results from the high concentration of aromatic compounds, all of which have very high octane values.

Any BTX needed for chemical use is separated from the reformat stream before it is blended into the gasoline pool. Although at a given refinery the total volume of gasoline production (eg, 16,000 m<sup>3</sup>/d) usually dwarfs the BTX volume (eg, 800 m<sup>3</sup>/d) and may have a higher priority, BTX production is often important enough to support its own reforming facilities and should not be considered simply as a gasoline by-product. This independence from gasoline may be even further emphasized in the future because of restrictions on the allowed level of BTX in gasoline and because new BTX processes may utilize light feeds or natural gas.

The need for BTX in gasoline has varied considerably. In the 1970s and 1980s in the United States, more high octane reformat was needed as the use of lead antiknock compounds was decreased for environmental reasons. More reforming capacity was put into use. Now there is environmental pressure to reduce the aromatic content (especially benzene) of gasoline (1). This may dramatically reduce production of gasoline reformat. Octane number requirements would have to be met with other high octane components such as oxygenated hydrocarbons (eg, methyl *t*-butyl ether (MTBE)). Therefore, the production of BTX for gasoline probably will drop. However, despite possible dislocations in supply, the demand for chemical uses will still be readily satisfied and the availability and price of BTX for chemical uses probably will not be greatly affected by the change in gasoline composition.

The principal chemical uses of BTX are illustrated in Figure 1 and listed in Table 1 (2). A very wide range of consumer products from solvents to fibers, films, and plastics are based on BTX. The consumption of BTX is approximately in the proportions of 67:5:28, respectively. However, no BTX process gives BTX in these proportions. The economic value of benzene and xylenes (especially *p*-xylene) is normally higher than that of toluene. Because of this, processes that convert toluene to benzene by hydrodealkylation (3) and disproportionate toluene to benzene and xylenes (4) have been commercialized. In addition, reforming processes that emphasize production of either benzene or *p*-xylene [106-42-3] have been described (5). Since these are not classified as BTX processes they are not discussed in detail here.

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**Fig. 1.** Principal uses of BTX.

### 1. Reforming

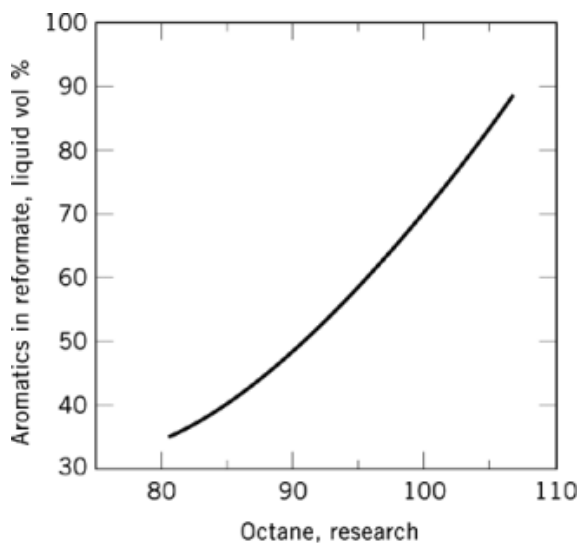
Reforming, as currently practiced, is a platinum-catalyzed high temperature vapor-phase process which converts a relatively nonaromatic C<sub>6</sub>–C<sub>12</sub> hydrocarbon mixture (naphtha) to an aromatic product called reformate (6). The catalyst often contains less than 1% of platinum, possibly modified with other metals, supported on a high surface area support such as alumina, which provides acidity (see Catalysis). The gasoline octane rating of the reformate is directly related to its aromatic content (Fig. 2). The aromatic content is higher when the reformer is operated at high severity (high temperature, low space velocity). Some cracking to light products also occurs, and this also increases at high severity. A typical reformate contains BTX in the proportions of 19/49/32, respectively, although these proportions can be varied by tailoring the feed composition. In response to the environmental pressure on benzene in motor gasoline mentioned previously, it is probable that many U.S. refiners will choose to reduce the proportion of benzene in their reformate by raising the cut point on the naphtha feed to their reformers.

#### 1.1. Feedstock

Feed for reformers is normally petroleum hydrocarbons that boil roughly in the 70–190°C range. When this feed (straight run naphtha) is obtained by fractionating a crude oil, its composition varies considerably with the source of the crude as shown in Table 2 (see Petroleum) (7). The aromatic content of these naphthas is

**Table 1. Consumption of BTX in the Manufacture of Chemicals, 1989, 10<sup>3</sup> t**

Product	Worldwide	United States
benzene		
cumene [98-82-8]	4,319	1,437
cyclohexane [110-82-7]	3,656	915
ethylbenzene [100-41-4]	10,863	3,248
all others	3,157	568
<i>Total (benzene)</i>	<i>21,995</i>	<i>6,168</i>
toluene		
cresol [1319-77-3]	93	
phenol [108-95-2]	271	36
toluene diisocyanate [1321-38-6] and	602	241
toluenediamine [26764-44-3]		
all others	564	194
<i>Total (toluene)</i>	<i>1,530</i>	<i>471</i>
<i>o</i> -xylene		
phthalic anhydride [85-44-9]	1,964	393
<i>p</i> -xylene		
dimethyl terephthalate [120-61-6]	2,349	870
terephthalic acid [100-21-0]	4,990	1,363
<i>Total (o- and p-xylene)</i>	<i>9,303</i>	<i>2,626</i>

**Fig. 2.** Octane rating as a function of aromatics in reformate.

quite low. Because of this and the lack of highly branched paraffins, the octane numbers are low. Also, some naphthas have high cycloparaffin (naphthene) contents. Since, in the reforming process, open chain paraffins first have to cyclize to cycloparaffins before they aromatize, those naphthas with high cycloparaffin content are generally easier to reform.

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**Table 2. Properties of Straight Run Naphthas from Various Crude Oils**

Crude properties			Naphtha properties					
Name (source)	Gravity, °API	Sulfur, wt %	Vol % of crude	Gravity, °API	Octane, research	Paraffins, wt %	Cyclo-paraffins, wt %	Aromatics, wt %
Arab Light (Saudi Arabia)	33.1	1.9	17.0	59.2	33.2	72	17	11
Arab Heavy (Saudi Arabia)	27.4	2.8	13.0	59.9	33.9	70	19	11
Iran Light (Iran)	33.5	1.4	17.8	56.2	45.9	59	28	13
Bonny Light (Nigeria)	34.3	0.1	16.1	51.9	63.0	37	51	12
Sumatra Light (Indonesia)	35.9	0.1	10.9	58.0	41.8	58	37	5
Ardjuna (Indonesia)	36.0	0.1	21.7	50.9	66.5	36	45	19
Brent (North Sea, UK)	38.2	0.4	20.2	54.0	62.3	47	39	14
Mayan (Mexico)	21.5	3.4	12.0	56.9	45.3	62	26	12
Isthmus (Mexico)	33.3	1.2	19.2	56.5	65.9	61	26	13
Alaska North Slope (Alaska, U.S.)	27.6	1.1	13.3	52.1	63.2	42	41	17
Huntington Beach (California, U.S.)	21.8	1.5	14.1	48.2	70.6	14	80	6
West Texas Intermediate (Texas, U.S.)	39.1	0.3	23.4	54.6	53.8	45	45	10
Empire Mix (Gulf Coast, U.S.)	32.3	0.3	12.7	52.4	61.2	43	44	13

In addition to straight run naphthas, 70–190°C cuts obtained by distillation from streams produced by cracking high boiling petroleum fractions can also be used as feed to reformers. Naphthas produced by hydrocracking are particularly suitable.

Impurities containing sulfur, nitrogen, and oxygen are undesirable in a reformer feed because they harm the catalyst. Therefore, these elements are largely removed by pretreating the feed with hydrogen (hydrotreating) in the presence of catalysts containing nickel–molybdenum, cobalt–molybdenum, or combinations (6). This process converts them into hydrogen sulfide, ammonia, and water, respectively, which are readily removed by distillation.

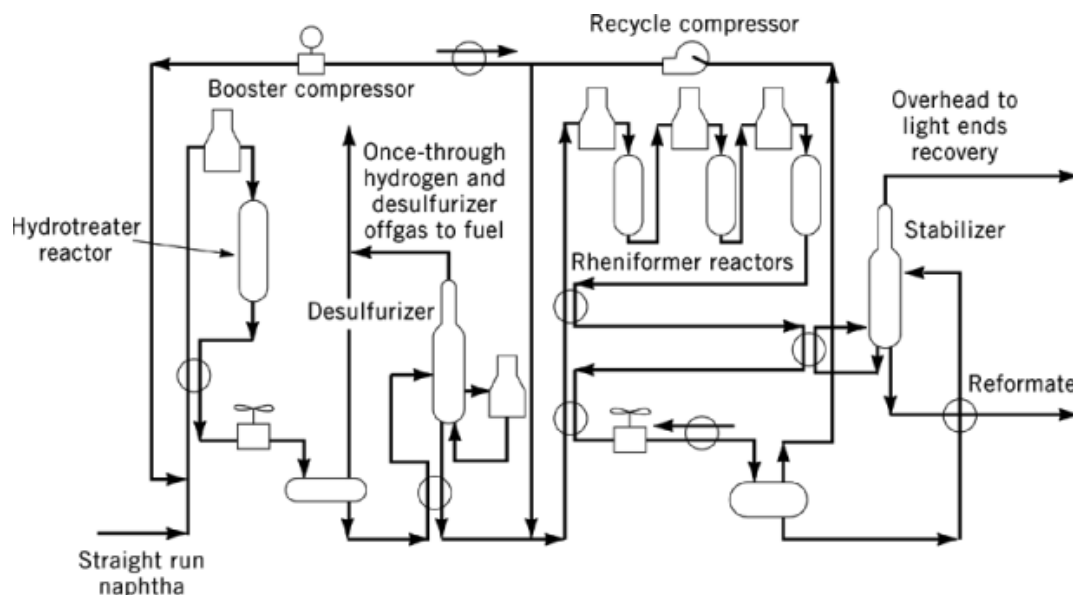
The molecular weight distribution of the feed affects the distribution of the product. If the naphtha is concentrated in the C<sub>6</sub>–C<sub>8</sub> range, more benzene and toluene are found in the product. If the feed is weighted to C<sub>8</sub>–C<sub>10</sub>, more xylenes and higher aromatics are found. Some carbon number “slippage” occurs by dealkylation: some C<sub>7</sub>s form benzene by losing a methyl group, some C<sub>8</sub>s form toluene, etc.

### 1.2. Reforming Conditions

The main process variables are pressure, 450–3550 kPa (50–500 psig), temperature (470–530°C), space velocity, and the catalyst employed. An excess of hydrogen (2–8 moles per mole of feed) is usually employed. Depending on feed and processing conditions, net hydrogen production is usually in the range of 140–210 m<sup>3</sup>/m<sup>3</sup> feed (800–1200 SCF/bbl). The C<sub>1</sub>–C<sub>4</sub> products are recovered and normally used as fuels.

A flow diagram for a typical semiregenerative reformer based on the Rheniforming Process (8) is shown in Figure 3. The hydrotreated feed is heat exchanged with the reformer product. Further heating is achieved by passage through a furnace. The feed then enters the first of several reactors which, in the Rheniforming Process, contain platinum–rhenium on alumina catalyst. To replenish the endothermic heat of reaction of the aromatization process, several sets (three are shown in Fig. 3) of alternating furnaces and reactors are used.

The excess hydrogen present actually inhibits aromatics formation but is necessary to reduce catalyst fouling by coke formation. Catalyst fouling is a critical issue in reforming. Process conditions and catalyst compositions balance conversion against fouling rate. Today, by using improved catalysts that foul more slowly



**Fig. 3.** Simplified process flow diagram of a naphtha hydrotreater and rheniformer.

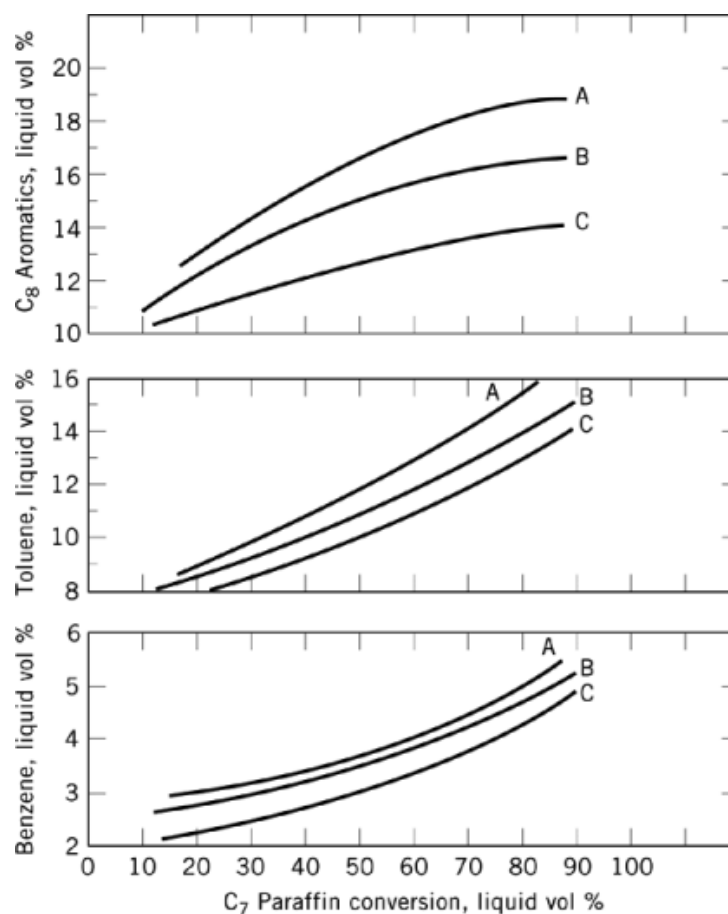
or by using continuous catalyst regeneration, commercial reformers can get high conversions and yields by operating at relatively low pressures, eg, 450–965 kPa (50–125 psig). Figure 4 shows the effects of pressure (mainly partial pressure of hydrogen) and of conversion on BTX yield.

As coke fouling occurs, the catalyst loses activity. Temperature must be raised to keep the conversion level constant. Typically only about a 20–30°C temperature rise is allowable. Then the very valuable platinum catalyst must be regenerated. Three approaches are used. If the run length (fouling time) is about six months or more, it is practical to shut down the unit and regenerate the catalyst in place. This approach, called semiregenerative reforming, is used in a number of commercial processes: Houdriforming, Magnaforming, Platforming, and Rheniforming (6).

If, because of feed type, process severity, or catalyst composition, the run length is short, the catalyst is regenerated in swing reactors or continuously. Processes using four to six reactors, one or more of which may be undergoing regeneration at any given time, have been developed, eg, Powerforming and Ultraforming (6). The catalyst has a higher average activity in these processes than in semiregenerative ones. Continuous regeneration is offered by UOP in the Continuous Catalyst Regeneration (CCR) Platforming Process, and by IFP in their Aromizing Process (9). A portion of the catalyst is continuously removed, regenerated in a separate regeneration loop, and returned to the reformer (see Catalysts, regeneration).

During regeneration the coke is burned off the catalyst. The techniques employed are fairly sophisticated so as to maintain the platinum and any other active metals in a well dispersed form and to restore the original catalyst activity. Regeneration usually takes several days.

The choice of reforming process depends on the product desired, plant size, and capital availability. If BTX is to be only a coproduct, the refiner might select a semiregenerative process. Severity is usually lower, and the important factor is the yield of gasoline. This yield for some combinations of feeds and catalysts can improve with successive catalyst regeneration cycles (10). For high BTX yields a swing reactor or continuous regeneration process might be the choice because BTX yields are highest at high severity and low pressure.



**Fig. 4.** Higher yields from lower pressures; reactor pressure: A, 791 kPa (100 psig); B, 1480 kPa (200 psig); C, 2515 kPa (350 psig). Data for Arabian Naphtha, 54–154°C fraction.

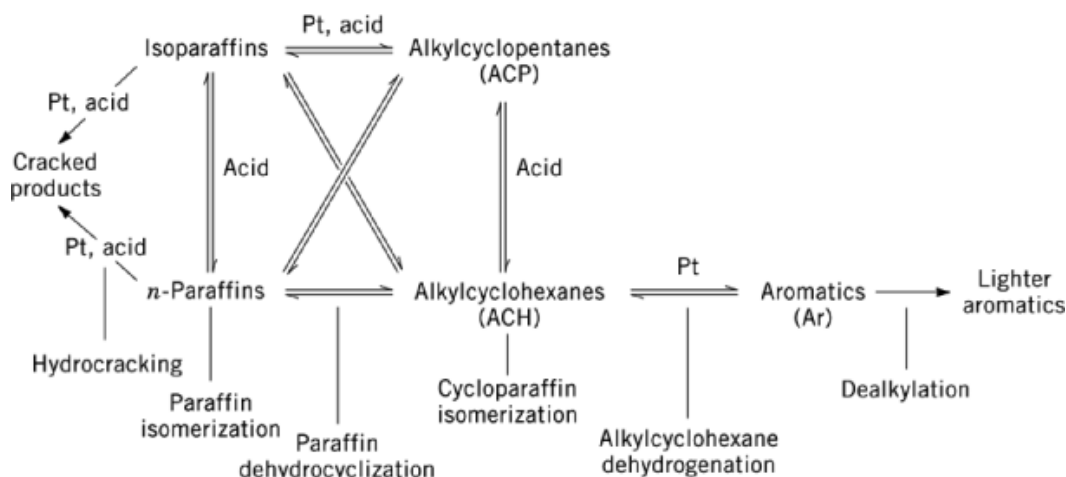
Patents cover a new reforming catalyst based on L-zeolite which gives a significantly higher yield of BTX, especially benzene, from light paraffinic feeds (11). Other new zeolites (12) may also offer advantages over the traditional reforming catalyst supports.

### 1.3. Reforming Chemistry

The main reactions occurring in a reformer are shown in Figure 5 (6, 13–15); most are reversible indicating the potential importance of reaction equilibrium.

In the alkylcyclohexane (ACH) to aromatic equilibrium,  $\text{ACH} \rightleftharpoons \text{Ar}$ , aromatics are favored by high temperatures and low pressures. Normal reforming conditions promote rapid ACH dehydrogenation and a high conversion to aromatics.

The alkylcyclopentane (ACP) to aromatics process ( $\text{ACP} \rightleftharpoons \text{ACH} \rightleftharpoons \text{Ar}$ ) is less efficient than ACH dehydrogenation, owing to the slowness of the first step and to ACP ring opening. Under conditions where cyclohexane is converted to benzene with close to 100% efficiency, only 50–75% of methylcyclopentane may be converted to benzene.



**Fig. 5.** Main reactions of catalytic reforming. Pt and acid refer to predominant active catalytic sites.

Aromatization of isoparaffins and *n*-paraffins is more difficult. Not only is the reaction slower, but also the ultimate yield is lower because more cracking occurs. Under mild reforming conditions a straight run naphtha with a high cycloparaffin (naphthene) plus aromatic content achieves a much higher octane rating (and aromatics content) than one with a high paraffin content. This latter naphtha can be more severely reformed to achieve a high octane rating, but then the yield of liquid product is lower.

## 2. Hydrocarbon Pyrolysis

A large amount of BTX is obtained as a by-product of ethylene manufacture (see Ethylene). The amount produced strongly depends on the feed to the ethylene plant. This is illustrated in Table 3 for various feeds to a typical large scale plant producing 450,000 t/yr of ethylene (16). Note that only about 1–2% of the ethane/propane feeds end up as BTX and it is almost completely benzene and toluene. As the feed goes up in molecular weight, the yield of BTX increases from 4% with butane feed to about 10% with gas oils, and the BTX proportions go from 72:20:8 respectively, to 44:34:22 respectively.

Outside the realm of typical hydrocarbon pyrolysis is the high temperature pyrolysis of methane. In one variant of this process, which has only been commercialized to produce acetylene (with some BTX), methane reacts in an electric arc at about 1500°C (17) with very short contact times. At higher temperatures or with a catalyst and added hydrogen, BTX is produced with fairly high selectivity (18).

## 3. BTX from Light Hydrocarbons

A completely new approach for BTX production has emerged in recent years. It converts C<sub>2</sub> to C<sub>6</sub> paraffins into aromatics using a modified ZSM-5 zeolite catalyst which contains gallium (19). An example of this approach, the Cyclar process, has been in commercial operation by British Petroleum at Grangemouth, Scotland since August 1990 (20). It uses C<sub>3</sub>–C<sub>4</sub> feed and employs UOP's CCR technology to compensate for rapid catalyst coking.

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**Table 3. BTX Yields from Various Pyrolysis Feeds,<sup>a, b</sup> 10<sup>3</sup> t/yr<sup>c</sup>**

Feed	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	Mid-crude naphtha	C <sub>6</sub> -C <sub>8</sub> Raffinate	Gas oil, distilled	
						Atm	Vac
ethylene	450	450	450	450	450	450	450
product rate							
feed rate	583	1080	1135	1349	1535	1750	2213
ethylene <sup>d</sup>	48.2	34.2	35.8	30.0	26.0	23.0	18.0
benzene	5.0	26.6	34.3	90.0	72.7	105.5	82.5
toluene	0.7	5.8	9.4	45.1	41.5	50.8	64.3
C <sub>8</sub> aromatics			4.0	23.8	18.4	38.0	41.4

<sup>a</sup>Ethane recycled to extinction.

<sup>b</sup>Ref. 16.

<sup>c</sup>Unless otherwise noted.

<sup>d</sup>Once through yield.

The mechanistic steps are as follows: paraffins dehydrogenate to olefins; the olefins oligomerize and cyclize; and the cyclics aromatize. Because the first step is rate controlling, very little olefin is actually present. The BTX product is relatively free of nonaromatics and therefore is very desirable as a chemical feed. As in reforming, some C<sub>1</sub>-C<sub>2</sub> fuel gas is produced along with a valuable hydrogen stream. From a C<sub>3</sub>-C<sub>4</sub> feed the BTX product is roughly 35:45:20, respectively.

### 4. Other BTX Processes

Because of the importance of the petroleum-based processes discussed previously, only about 1% of the U.S. supply of BTX currently comes from coal pyrolysis (21).

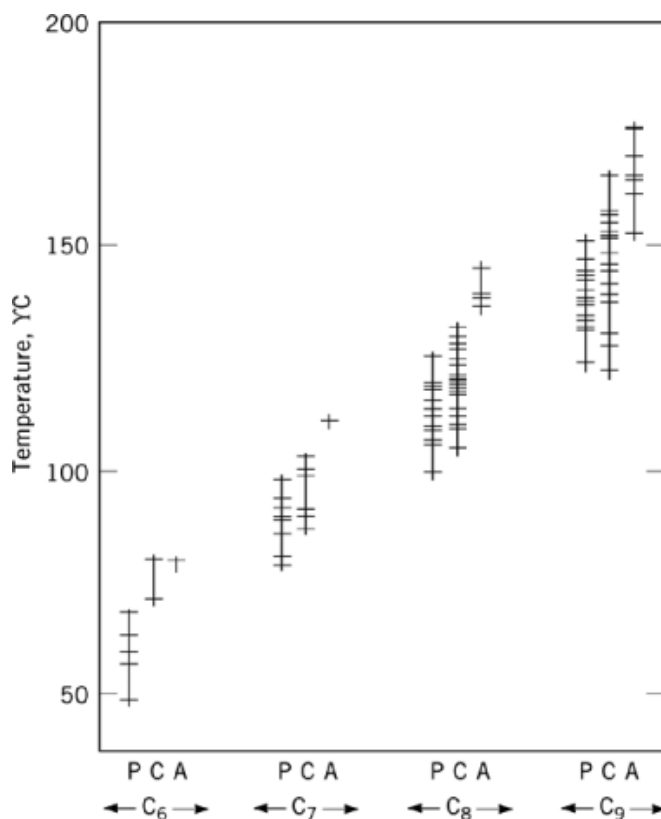
Outside the United States, coal pyrolysis is more important as a source of BTX. The proportions are about 70:20:10, but can vary greatly depending on the coal and on the pyrolysis process used. Product quality is not as good as petroleum-derived BTX. This source could become more important again if petroleum costs escalate. Much higher yields of BTX from coal can be obtained by first hydrogenating the coal (22).

Another very interesting route to BTX is the Mobil Methanol To Gasoline (MTG) Process (23). Methanol is converted into gasoline containing about 50% aromatics by passing it over a ZSM-5 catalyst. The BTX composition is about 10:20:70, respectively. More than half of the aromatics present are C<sub>9</sub>s and C<sub>10</sub>s, and these would have to be dealkylated to yield more BTX. The methanol can be obtained from any syngas source such as coal, natural gas, or petroleum (see Methanol). The economic attractiveness of this approach depends on the cost of methanol relative to gasoline from petroleum. A commercial plant has been operating successfully since 1985 in New Zealand where natural gas is abundant and petroleum is scarce (24).

### 5. BTX Recovery

The complexity of separating and purifying the individual BTX components from crude BTX products depends on the amount of nonaromatic impurities present. If the amount is small enough, simple distillation can suffice. If not, it is obvious from Figure 6 that distillation alone will not be sufficient because the BTX aromatic compounds are close in boiling point to some of the cycloparaffins of the same carbon number or to paraffins of the next higher carbon number. Because of this, extraction or extractive distillation with a polar solvent





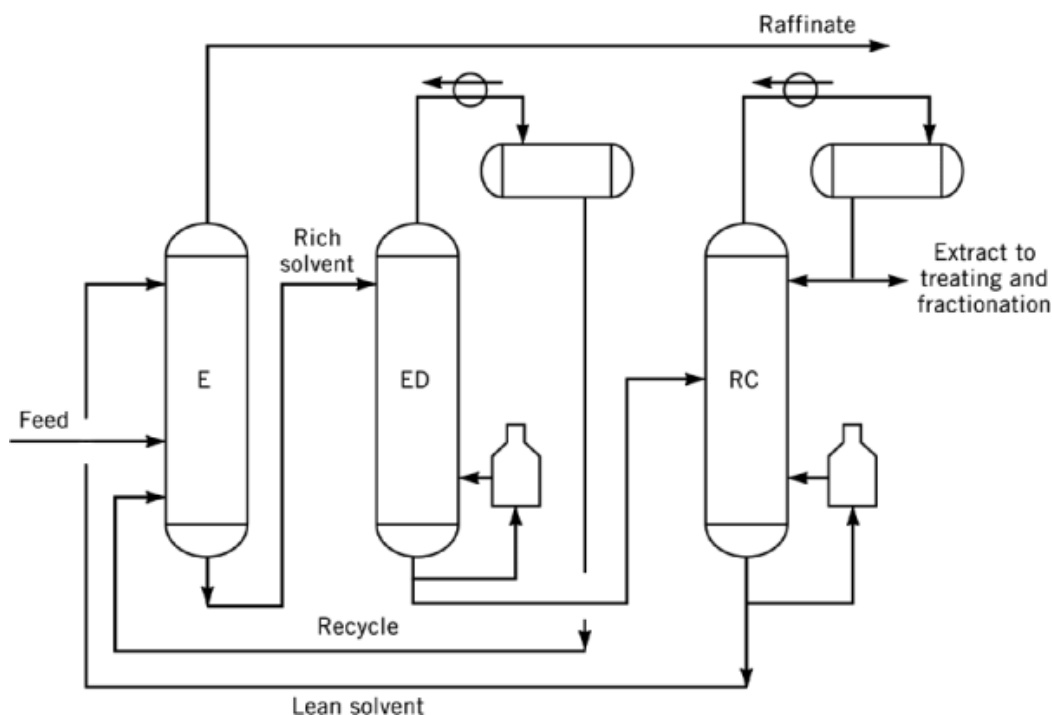
**Fig. 6.** Boiling points of C<sub>6</sub>–C<sub>9</sub> hydrocarbons. P, iso and normal paraffins; C, C<sub>5</sub>- and C<sub>6</sub>-cycloparaffins; and A, aromatics.

is used to separate the slightly polar aromatic hydrocarbons from the nonpolar nonaromatic hydrocarbons. When olefins are also present, as in pyrolysis gasoline, these interfere with the extraction and must first be hydrogenated or removed by adsorbents.

An option for avoiding the cost of extraction is to increase the severity of the BTX formation step. This reduces the quantity of residual paraffins, and, depending on the BTX formation process, may leave the BTX clean enough to purify by distillation. The final impurity concentrations may still be too high for merchant sale, but may be acceptable in some downstream operations. For example, xylenes going into an isomerization/separation loop for *p*-xylene production can contain some paraffins if the isomerization catalyst is capable of decomposing them. Disadvantages of high severity processing are the increased catalyst fouling rate and the potential increase in undesirable olefin impurities.

### 5.1. Extraction and Extractive Distillation

The choice of an extraction or extractive distillation solvent depends upon its boiling point, polarity, thermal stability, selectivity, aromatics capacity, and upon the feed aromatic content (see Extraction). Capacity, defined as the quantity of material that is extracted from the feed by a given quantity of solvent, must be balanced against selectivity, defined as the degree to which the solvent extracts the aromatics in the feed in preference to paraffins and other materials. Most high capacity solvents have low selectivity. The ultimate choice of solvent



**Fig. 7.** Shell sulfolane extraction process. E, extraction; ED, extractive distillation; RC, recovery column. Courtesy of UOP, Inc.

is determined by economics. The most important extraction processes use either sulfolane or glycols as the polar extraction solvent.

Sulfolane [126-33-0], used in UOP and Shell processes (25, 26), offers good thermal and hydrolytic stability, high density and boiling point, and a good balance of solvent properties. Its high density and boiling point make it easy to separate from the hydrocarbon streams. A diagram of a sulfolane extraction unit is shown in Figure 7. Fresh feed enters the extractor and flows countercurrent to the down flowing solvent. The raffinate is withdrawn at the top of the extractor and leaves the system after water washing. The solvent, now rich in aromatics, is sent to the top of the extractive stripper where the nonaromatic hydrocarbons are removed. Aromatics and sulfolane are separated in the recovery column. The lean solvent is recycled to the extractor and the aromatics are washed with water and removed. The recovery of benzene and toluene is usually 99+%; of  $C_8$  aromatics 97%; and of  $C_9^+$  aromatics 75–90%.

The widely employed UOP Udex Process uses a glycol solvent (27). Diethylene glycol was used in early versions of the process; however, increased capacity was obtained by adding dipropylene glycol or, in some cases, a change was made to triethylene glycol. Further improvement was made by using tetraethylene glycol (28). The Union Carbide Tetra Process also employs tetraethylene glycol (29). Other extraction processes are included in Table 4.

Extractive distillation, using similar solvents to those used in extraction, may be employed to recover aromatics from reformates which have been prefractionated to a narrow boiling range. Extractive distillation is also used to recover a mixed benzene–toluene stream from which high quality benzene can be produced by postfractionation; in this case, the toluene product is less pure, but is still acceptable as a feedstock for

**Table 4. Extractive Processes for BTX Recovery**

Company process	Solvent	CAS Registry Number	Reference
<i>Extraction</i>			
Shell Process	sulfolane	[126-33-0]	(25, 26)
UOP Udex Process	diethylene glycol	[111-46-6]	27
	triethylene glycol	[112-27-6]	
	tetraethylene glycol	[112-60-7]	28
	tetraethylene glycol	[112-60-7]	29
Union Carbide Tetra Process			
Lurgi Arosolvan	<i>N</i> -methyl-2-pyrrolidinone	[872-50-4]	(30, 31)
	and monoethylene glycol	[107-21-1]	
Institut Français du Pétrole	dimethyl sulfoxide (DMSO)	[67-68-5]	32
SNAM Progetti Formex	<i>N</i> -formylmorpholine	[4394-85-8]	33
Howe-Baker Aromex	diglycolamine	[929-06-6]	34
Krupp-Koppers Morphylex	<i>N</i> -formylmorpholine	[4394-85-8]	35
<i>Extractive distillation</i>			
Institut Français du Pétrole DMF	dimethylformamide (DMF)	[68-12-2]	5
Krupp-Koppers Octenar	<i>N</i> -formylmorpholine	[4394-85-8]	5
Lurgi Distapex	<i>N</i> -methyl-2-pyrrolidinone	[872-50-4]	5
UOP Sulfolane	sulfolane	[126-33-0]	5

dealkylation or gasoline blending. Extractive distillation processes for aromatics recovery include those listed in Table 4.

## 5.2. Downstream Processing

In addition to extraction, various downstream operations are often carried out on the BTX product to produce products in proportions to fit the market demand. A typical aromatics processing scheme is shown in Figure 8 in which benzene, *p*-xylene, and *o*-xylene are the products.

After the crude BTX is formed, by reforming in this case, a heart cut is sent to extraction. Actually, the xylenes and heavier components are often sent to downstream processes without extraction. The toluene produced is converted to benzene, a more valuable petrochemical, by running it through a hydrodealkylation unit. This catalytic unit operates at 540–810°C with an excess of hydrogen. Another option is to disproportionate toluene or toluene plus C<sub>9</sub> aromatics to a mixture of benzene and xylenes using a process such as UOP's Tatoray or Mobil's Selective Toluene Disproportionation Process (STDP) (36).

The *o*-xylene [95-47-6] in Figure 8 is recovered by a two-stage distillation. First it is separated (or split) from *m*-xylene [108-38-3] and the other C<sub>8</sub> aromatics in a superfractionating column, the xylene splitter, (Unit H). The bottoms, a mixture of *o*-xylene and C<sub>9</sub><sup>+</sup> aromatics, is redistilled (or rerun) in Unit I to recover *o*-xylene of 96+% purity.

The distillate (overhead) from Unit H, containing mostly ethylbenzene [100-41-4], *p*-xylene, and *m*-xylene, and some *o*-xylene becomes the feed for the *p*-xylene separation process (Unit J).

*p*-Xylene [106-42-3] can be purified by crystallization or adsorption. When a typical reformate-derived C<sub>8</sub> aromatic mixture is cooled, *p*-xylene crystallizes first. Most plants employing crystallization operate at –60 to –75°C, depending on feed composition (37). The process is limited by a eutectic temperature below which *o*- or *m*-xylene also crystallize. The solubility of *p*-xylene in the remaining C<sub>8</sub> aromatic mixture over the range of –60 to –75°C is 9.6 to 6.2%.

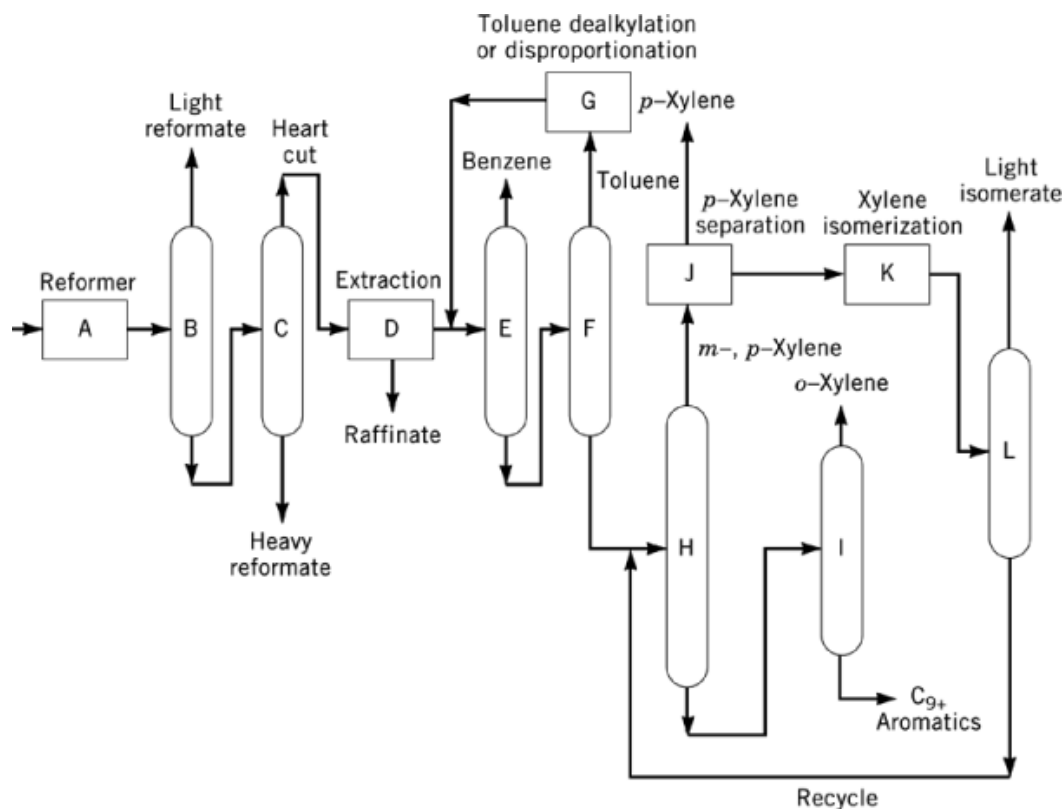


Fig. 8. General BTX processing sequence.

UOP's ParexProcess can be used to purify *p*-xylene by adsorption (38). Toray has a similar process. These processes take advantage of the fact that *p*-xylene is adsorbed more easily than the other C<sub>8</sub> aromatics by a suitable molecular sieve. The *p*-xylene is desorbed by either a lighter or heavier hydrocarbon which is subsequently removed by distillation. *p*-Xylene is recovered in about 97% yield (see Adsorption).

The mother liquor obtained from the crystallization, or the raffinate after removal by adsorption, is isomerized using an acidic catalyst to convert *m*-xylene to the *o*- and *p*-isomers (Unit K in Fig. 8).

In the isomerization step, light and heavy impurities are generated, including saturated hydrocarbons, benzene, toluene, and C<sub>9</sub><sup>+</sup> aromatics. These are removed by recycling the isomerate through the xylene splitter and the light isomerate column (Unit L). If the light isomerate contains much benzene or toluene, it can be recycled to Unit G. *m*-Xylene may be recovered between the xylene splitter and the *p*-xylene separation plant by selective sulfonation followed by regeneration or via complex formation with a mixture of HF and BF<sub>3</sub> (39).

To this point the presence of ethylbenzene in the mixed xylenes has been ignored. The amount can vary widely, but normally about 15% is present. The isomerization process must remove the ethylbenzene in some way to ensure that it does not build up in the isomerization loop of Figure 8. The ethylbenzene may be selectively cracked (40) or isomerized to xylenes (41) using a platinum catalyst. In rare cases the ethylbenzene is recovered in high purity by superfractionation.

There are many variations of the basic processing loop shown in Figure 8. Processing to produce only BT is common, often in conjunction with a toluene-to-benzene dealkylation unit. If benzene and toluene are not to be recovered, Column B may be used to remove toluene and lighter components. In that case, Units E, F,

and G would be eliminated. To recover *p*-xylene only, the xylene splitter is reduced in size and is used to split between *o*-xylene and the C<sub>9</sub><sup>+</sup> aromatics. The *o*-xylene rerun still is then eliminated.

## 6. Environmental Considerations

BTX processing has come under steadily increasing pressure to reduce emissions and workplace exposures (see Industrial hygiene). Reductions in the permissible levels of both benzene and total aromatics (BTX) in gasoline have been legislated. Whereas all BTX components are to be controlled, the main focus is on benzene because it is considerably more toxic than the others and is classified as a known carcinogen (42).

Workplace exposure limits for benzene have been regulated to levels as low as 0.5 ppm (43). Industrial emissions affecting the public are now low enough that the EPA considers that a greater hazard exists from mostly indoor sources such as smoking, automobile exhausts, and consumer products (44).

The stringent controls over manufacturing and handling benzene may dissuade refiners from installing new equipment to extract benzene from gasoline to satisfy gasoline requirements. Instead they will probably modify their reforming operations to produce less benzene or to convert the remaining benzene to other compounds. They will achieve the necessary octane rating for gasoline via branched paraffins and oxygenates. Overall, this is likely to result in further segregation of petrochemicals BTX production from gasoline production.

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Benzene; Toluene; Xylenes and ethylbenzenes; Gasoline