

PRESENT AND FUTURE SUPPLY OF COAL CHEMICALS FROM PETROLEUM SOURCES

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In a discussion of the chemistry and the supply of coal chemicals from petroleum sources, it is essential to define the terminology. In this discussion, coal chemicals will include:

- I The light oil fraction boiling up to 200°C and including primarily benzene, toluene and the mixed xylenes.
- II The middle oil fraction, boiling point (BP) 200-250°C, one of the major components of the total liquid fraction, consisting of tar acids such as phenol, cresols, xyleneols as well as higher tar acids. This fraction also contains tar bases such as quinoline. The major component of the middle oil fraction is naphthalene and methylnaphthalene.
- III The heavy oil fraction, BP 250-300°C, containing dimethylnaphthalenes and acenaphthene.
- IV The anthracene oil, BP 300-350°C, containing fluorene, phenanthrene, anthracene and carbazole.

A. Light Oil - Supply Aspects

1. Benzene

Until 1950, benzene produced from coke-ovens and by tar distillers was sufficient for chemical requirements, with imports helping to supply peak demands. When military requirements increased rapidly during the Korean "emergency" and by-product coke-oven capacity was inadequate, petroleum refiners stepped in to take up the slack. The first benzene produced from petroleum appeared in 1950, and in 1961 petroleum benzene accounted for better than 75% of the total production. Table 1 presents historical data on the production and sales of benzene.

The end-use pattern of benzene given in Table 2 is quite extensive, with the main markets being in styrene, phenol, synthetic fibers and synthetic detergents. There will be some market changes, however. Use of benzene to make nylon and detergents has been levelling off at an annual growth rate of 3 to 5%. In the future, the big markets will be styrene and phenol.

In 1961, benzene production and sales were 545 and 431 million gallons, respectively. It is expected that by 1971, production will amount to approximately 840 million gallons, a 4.4% annual increase. The past and estimated future benzene production figures are presented graphically in Figure 1.

Table 1 - BENZENE PRODUCTION AND SALES, 1950-1961

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	22.0	162.2	10.1	194.3	172.6
1951	19.0	178.0	32.6	229.5	239.2
1952	19.0	155.1	35.5	209.6	217.0
1953	19.0	178.8	63.0	260.8	232.7
1954	15.0	142.8	91.9	249.7	202.0
1955	15.0	174.2	98.6	287.8	264.8
1956	15.0	174.4	111.6	301.0	284.5
1957	13.0	181.1	116.2	310.2	276.5
1958	9.0	119.8	142.1	270.8	243.3
1959	10.0	120.3	208.8	339.1	330.5
1960	12.8	135.3	309.2	457.3	377.4
1961	12.4	120.2	412.8	545.4	431.0

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Table 2 - BENZENE END-USE PATTERN AS OF 1960

	Percent of Total
Aniline	4.1
Benzene Hexachloride	0.4
DDT	4.1
Maleic Anhydride	2.8
Nylon	7.8
Phenol	23.4
Styrene	47.4
Synthetic Detergents	7.0
Dichlorobenzene	2.3
Other Non-Fuel Uses	0.5
Motor Grade	0.2
	<u>100.0</u>

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2. Toluene

Toluene from petroleum sources has attained a very important status in the past decade. Of the 260 million gallons of toluene produced in 1961, 88% were petroleum derived, with the remainder supplied by coke-ovens and tar distillers. In 1950, petroleum toluene accounted for only 54% of the 84 million gallons produced. Table 3 presents historical production-sales trends for toluene.

The largest end-use for toluene as of 1960, as shown in Table 4, is as a high octane blending agent in motor and aviation gasolines. This outlet, however, is declining rapidly because of the advent of jet aircraft and the emphasis on regular-gasoline economy. These facts, along with a benzene shortage, combined for a time to create a disposal problem for refiners and made the conversion of toluene into benzene by hydrodealkylation an attractive process. This has resulted in an increase in benzene production which has satisfied the present demand. Other uses of

Table 3 - TOLUENE PRODUCTION AND SALES, 1950-1961

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	7.7	30.7	45.5	83.9	70.3
1951	11.4	34.3	55.7	101.4	82.4
1952	10.8	30.5	64.0	105.3	87.5
1953	4.7	36.0	115.5	156.2	90.9
1954	2.9	33.4	122.9	159.2	126.2
1955	3.9	38.2	143.4	185.5	138.3
1956	5.6	37.2	130.8	173.6	135.2
1957	4.7	38.0	154.9	197.6	130.0
1958	4.2	28.0	207.4	239.6	136.6
1959	3.7	26.9	251.0	281.6	166.8
1960	3.2	30.4	240.8	274.4	200.1
1961	3.1	28.5	228.3	259.9	162.9

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Table 4 - TOLUENE END-USE PATTERN AS OF 1960

	Percent of Total
Motor Gasoline	50.5
Aviation Gasoline	18.6
Solvents (chiefly for Nitrocellulose Lacquers)	13.6
TNT	2.3
Detergents (Toluene Sulfonates)	1.8
Toluene Diisocyanate	1.4
Benzene*	0.4
Miscellaneous Chemicals (Benzoic Acid, Benzaldehyde, Benzoyl Chloride, Phenol, etc.)	11.4
	100.0

* In 1961, with the installation of many hydrodealkylation units by various companies, the consumption of toluene for benzene production was expected to increase to 60 million gallons. 1960 consumption was 1 million gallons.

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toluene shown in Table 4 are in the manufacture of chemicals, such as toluene diisocyanate and toluene sulfonate, and as a solvent for paints and nitrocellulose lacquers.

The present requirements of toluene also appear to be met. However, the development of additional processes, such as Dow's phenol-from-toluene process and DuPont's caprolactam-from-toluene process may play a major role in increasing the demand for more toluene. It is expected that by 1971, toluene production will amount to 450 million gallons, a 5.6% yearly increase. The past and estimated future toluene production figures are also presented in Figure 1.

3. Xylenes

The xylene aromatics are coal-tar chemicals which are also derived from petroleum and are being extracted by refiners and separated for chemical consumption to an increasing extent. Of

the 257 million gallons of mixed xylenes produced in 1961, 96.9% were derived from petroleum, 2.9% from coke-ovens and 0.2% from tar distillers, as will be seen from Table 5.

Table 5 - MIXED XYLENES PRODUCTION AND SALES, 1950-1961.

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	1.5	8.0	62.4	71.9	56.4
1951	2.2	9.1	64.4	75.7	58.5
1952	2.1	8.1	61.6	71.8	57.8
1953	0.7	9.9	102.9	113.5	65.6
1954	0.5	10.0	99.7	110.2	66.5
1955	0.6	11.3	96.1	108.0	77.6
1956	1.9	10.3	124.1	136.3	85.3
1957	1.3	10.8	115.1	127.2	83.0
1958	0.6	8.4	191.5	200.5	95.1
1959	0.5	7.5	233.5	241.5	128.8
1960	0.4	8.1	274.0	282.5	141.5
1961	0.5	7.6	249.2	257.3	124.0

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The major outlets for xylenes are in fuels, solvents and chemical uses, shown in Table 6. Gasoline octane improvement is the largest outlet for xylenes, and nothing will change this for a long time. Xylenes face the same problems as toluene, with aviation gasoline demand decreasing and motor gasoline needs being somewhat indefinite at the present time. Solvent uses claim approximately 17% of the mixed xylenes production.

Table 6 - XYLENES END-USE PATTERN AS OF 1960

	Percent of Total
Gasoline	61.0
Solvents	17.5
<u>ortho</u> -Xylene	6.3
<u>meta</u> -Xylene	1.7
<u>para</u> -Xylene	9.6
Miscellaneous Chemicals (Herbicides, Plasticizers, Chlorinated Xylene, etc.)	3.9
	<u>100.0</u>

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For chemical synthesis, the xylenes fraction is separated into the pure isomers -- ortho, meta, and para -- the consumption of which is shown in Table 7 for 1959 - 1961. Ethylbenzene is also obtained during the separation process. Composition of a petroleum derived mixed-xylenes stream is variable but generally contains the three isomers and ethylbenzene in the following proportions:

Ethylbenzene	8.6 - 13.2 %
<u>para</u> -Xylene	17.1 - 20.3 %
<u>meta</u> -Xylene	45.5 - 52.2 %
<u>ortho</u> -Xylene	18.0 - 24.4 %

Table 7 - XYLENE ISOMERS CONSUMPTION 1959 - 1961

Year	Millions of Gallons		
	Consumption		
	<u>ortho-Xylene</u>	<u>meta-Xylene</u>	<u>para-Xylene</u>
1959	8.4	2.1	22.0
1960	16.3	4.4	24.8
1961	22.3	5.5	26.5

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a. Para-Xylene

Para-xylene is currently the most important of the xylene isomers. Recent production of para-xylene is 280 million pounds (39 million gallons) per year. It is used primarily to make terephthalic acid which is usually sold as the dimethyl terephthalate ester for the production of polyesters such as DuPont's Dacron fiber and Mylar film.

b. Ortho-Xylene

Ortho-xylene is the second-most important isomer and could become another major feedstock for phthalic anhydride, now that improved catalyst and plant designs have increased yields to a respectable level. In the past, ortho-xylene was considered a poor substitute for naphthalene because the yield was only half of the theoretical of 1.39 lb/lb of feed, while naphthalene yielded three-fourths of the 1.16 lb/lb theoretical. Present ortho-xylene capacity is 650 million pounds per year. About 80% of the future production from these facilities is destined for export to Europe and Japan where it will be used to make phthalic anhydride.

c. Meta-Xylene

The most plentiful isomer, meta-xylene, which makes up about 50% of the xylene isomer mixture, is the least useful. Meta-xylene is used to make isophthalic acid, which competes with phthalic anhydride for the reinforced plastic and plasticizer market. One refiner separates meta-xylene for isophthalic acid production and another produces isophthalic from mixed xylenes along with terephthalic acid. The chief use for meta-xylene is for solvent and gasoline blending after the more valuable xylenes have been extracted.

The past and estimated future production figures for xylenes are shown graphically in Figure 1.

B. Light Oil - Chemistry and Chemical Engineering Aspects

The chemistry and chemical engineering of the production of light oil aromatics from petroleum are of considerable interest. The problem is that of the conversion of a suitable raw material and the separation of the aromatics from the residual paraffinic and naphthenic hydrocarbons. Although the chemistry of the production of benzene from petroleum sources is very similar to that of the production of toluene and xylenes, some subtle differences do exist in both chemical and the chemical engineering aspects of the problem.

In the case of benzene, a suitable raw material is one which contains substantial proportions of cyclohexane and methylcyclopentane. Table 8 shows the composition of the fraction which contains the two benzene precursors in various straight-run gasolines.⁽¹⁾ It will be observed that the total naphthenes will vary from approximately 20 to about 55 percent of the total fraction and

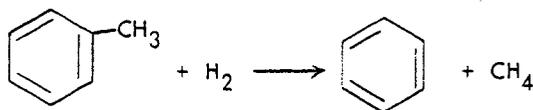
this fraction in return ranges from about 10 to 18 percent of the total C₅ to 360°F gasoline. This table indicates that the potential benzene production from straight-run gasoline is extremely high, to say nothing of the substantial amounts of methylcyclopentane and cyclohexane being currently produced synthetically by the hydrocracking processes which are now coming into commercial operation.

Table 8 - COMPOSITION OF 140-185°F FRACTIONS FROM VARIOUS STRAIGHT-RUN GASOLINES

Hydrocarbon, Vol.-%	Source						
	Ponca City Okla.	East Texas	Bradford Pa.	Greendale Mich.	Winkler Texas	Midway Calif.	Conroe Texas
2-Methylpentane	9	15	22	7	17	14	11
3-Methylpentane	8	12	13	5	42	10	8
n-Hexane	41	31	37	63	11	16	17
2, 2 & 2, 4-Dimethylpentane	2	6	6	2	8	4	3
Methylcyclopentane	20	23	9	9	15	34	21
Cyclohexane	16	12	12	11	6	21	31
Benzene	4	1	1	3	1	1	9
Total Naphthenes	36	35	21	20	21	55	52
Percent of 140-185°F Fraction Based on C ₅ -360°F Gasoline	13	16	15	18	10	12	14

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As mentioned earlier, some benzene is also produced by the hydrodealkylation of toluene. Various processing schemes have been proposed. The Hydeal* process is a catalytic operation which converts toluene concentrates into benzene in the presence of recycled hydrogen. Since the process consumes hydrogen in the formation of benzene and methane, as shown by the equation:

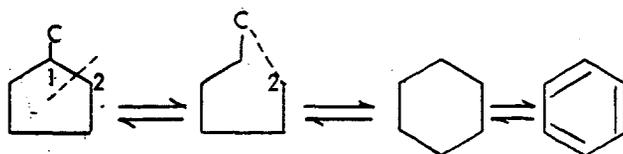


the units are equipped with internal hydrogen enrichment facilities so that the available hydrogen in the make-up gas can be utilized efficiently.

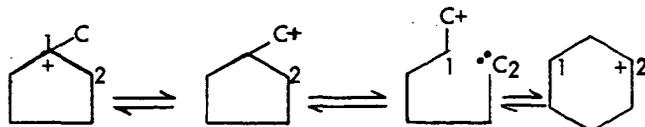
Another possible source of benzene is represented by the normal hexane which is a substantial component of the straight-run fractions. In fact, some of the early work in catalytic reforming has been directed on the dehydrocyclization of normal hexane to benzene and normal heptane to toluene. However, it should be pointed out that under conditions which induce a very high conversion of the naphthenic hydrocarbons to benzene, the conversion of hexane to benzene is very slight. Consequently, the bulk of the benzene is derived at the present time by processing fractions containing methylcyclopentane and cyclohexane.

The chemistry of the conversion of cyclohexane and methylcyclopentane is of considerable interest. Cyclohexane can be converted to benzene in the presence of a platinum-containing catalyst at exceedingly high rates. However, under the same conditions, methylcyclopentane is virtually unreacted. The reason for this lies in the need for rearrangement of the methylcyclopentane molecule to a cyclohexane intermediate prior to the conversion to benzene. This rearrangement reaction requires a bond breakage and the formation of a new bond as shown in the following:

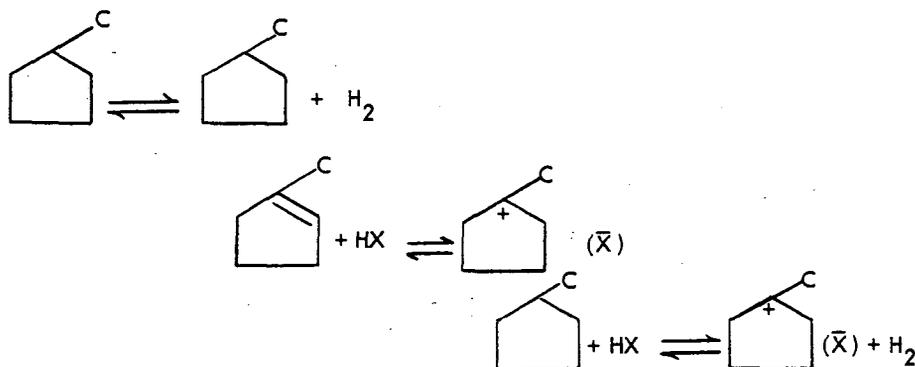
* Trademark



In detail, the carbonium ion mechanism which is involved in such a rearrangement calls for the formation of a tertiary carbonium ion with the subsequent shift to a primary carbonium ion and its addition at the second carbon atom, thus effecting the ring closure:



It will be observed that a cyclohexyl carbonium ion is produced. It is converted to cyclohexane in the reverse manner of the initial formation of the methylcyclopentane carbonium ion:



As pointed out above, in the absence of an acid catalyst no reaction of methylcyclopentane will take place, and a so-called bi-functional catalyst is required. This bi-functional property implies the balanced presence of both dehydrogenation-hydrogenation and acid activities. The proper balance is quite critical; otherwise, methylcyclopentane may be converted directly into hexane instead of cyclohexane.

We have found that a balanced catalyst is obtained by a specially prepared composite of aluminum, platinum and halogen, such as fluorine or chlorine. The conversion of methylcyclopentane is then readily carried out at about 450-500°C and about 20 atmospheres pressure in the presence of recycle hydrogen. The dehydrogenation under pressure in the presence of recycle hydrogen is now well-established in petroleum technology. Under these conditions, a clean catalyst surface is maintained so that long on-stream times are readily achieved.

It should be further pointed out at the conditions of operation the thermodynamic equilibrium among the three species, cyclohexane, methylcyclopentane and benzene, are such that the end product should contain a substantial amount of benzene, a very small amount of cyclohexane and an intermediate amount of methylcyclopentane. Therefore, it is imperative that there be a rapid conversion of the cyclohexane to benzene, so that methylcyclopentane may be converted into cyclohexane and the latter removed from the system in the form of benzene as rapidly as possible.

Unless this is done, methylcyclopentane cannot be converted into cyclohexane and will undergo undesirable side reactions such as the formation of hexanes.

The argument may be raised regarding the existence of the cyclohexane intermediate in the conversion of methylcyclopentane into benzene. In connection with this, we have carried out a study which provides a reasonable answer to the problem. This study involved the poisoning of the catalyst system by means of sulfur and observing the effect of the poison upon the conversion of cyclohexane and methylcyclopentane. The rate of cyclohexane conversion is normally much greater than that of methylcyclopentane. Therefore, if the cyclohexane rate is poisoned, the methylcyclopentane rate should not be affected until the cyclohexane rate is poisoned to the extent that it falls below the normal methylcyclopentane rate. This is essentially what has been found experimentally, as will be observed from Figure 2. Thus the indications are that at least the same intermediate is involved in the conversion of both cyclohexane and methylcyclopentane.

As might be expected, the conversion of C₇ and C₈ naphthenes into toluene and xylenes, respectively, also proceeds very readily over the bi-functional catalyst. It should be pointed out that, as the molecular weight is increased, the rate of the conversion of C₅ ring naphthenes rises rapidly. This is quite understandable on the basis of a considerably increased number of possible carbonium ions. The same is true for paraffinic hydrocarbons, so that higher aromatics are readily obtained from higher paraffins by the dehydrocyclization reaction.

It should be mentioned that under the usual operating conditions, the bi-functional catalyst will effect an equilibration among the isomers of the higher aromatics, so that the product will exhibit a composition closely approximating the thermodynamic equilibrium. However, it is possible to reduce the extent of equilibration by a proper selection of charging stock and operating conditions. Although ethylbenzene is not truly a coal chemical, it is an important intermediate for the production of styrene, and is normally prepared by the alkylation of benzene with ethylene.

With almost half of the benzene market going to styrene manufacture, refiners are taking a closer look at ethylbenzene separation from xylene by super-fractionation to compete with benzene alkylation as a styrene intermediate. Ethylbenzene from this source has a maximum potential of only 70 million gallons (505 million pounds) per year based on present xylene production and cannot replace benzene as a styrene feedstock but could take a share of the market. Economics of ethylbenzene separation depends greatly on the concentration of ethylbenzene in the mixed aromatics, which varies from crude to crude.

In one of our studies on ethylbenzene, we have investigated the possibility of producing ethylbenzene in high concentrations from straight-run fractions. Ethylbenzene is unique in one respect and that is that its direct precursor, ethylcyclohexane, is the highest boiling C₈ naphthene. Thus, by proper selection of the charging stock and operating conditions which do not cause excessive equilibration, it is possible to attain high ethylbenzene concentrations in the product.

The following procedure was employed. A so-called pre-xylene fraction in the Engler boiling range of 123 to 132°C was hydrogenated and subsequently distilled into 20 cuts. Each cut was processed over the bi-functional catalyst and the aromatic product distribution was determined. The following is the summary of the results:

Cut No.	BP, °C	Percent Distribution of the Aromatic Portion			
		p-Xylene	m-Xylene	o-Xylene	Ethylbenzene
1	116.8	24.9	58.3	16.8	0
5	122.0	21.6	55.9	20.3	2.2
10	126.5	13.2	34.7	33.1	19.0
14	131.1	2.5	4.1	13.5	79.9
15	132.6	2.6	0.3	14.0	83.1
16	133.9	1.1	1.9	7.6	89.9
17	134.9	1.6	2.0	8.5	87.9

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It will be observed that very high concentrations of ethylbenzene may be produced directly. Since ortho-xylene is the main impurity at the high concentrations of ethylbenzene, it can be readily separated to produce ethylbenzene fractions having a purity in excess of 95%. The above example serves to demonstrate the high versatility of a method involving variations in charging stock, catalyst and operating conditions.

The presence of a substantial number of hydrocarbons which may be converted into specific aromatic compounds has as one drawback the variable amounts of other charging stock components which remain in the aromatic product. Thus, the extremely rapid rise in the rate of production of lower aromatics would not be possible without the concurrent development of methods of separation of these aromatics from the other hydrocarbon components. These methods involve extraction by liquids and solids. One method which has received wide commercial acceptance is the Udex^(R) process,⁽²⁾ which employs a glycol-water mixture as a selective solvent. Originated by Dow Chemical Company and developed by Universal Oil Products Company, this process combines a high selectivity with a minimum utility requirement. Aromatics are recovered as a hydrocarbon type with a subsequent fractionation to produce pure benzene, toluene and mixed xylenes. It is interesting that the selectivity of separation is highest for benzene and decreases with increasing molecular weight.

C. Hydrocarbon Components Of Higher Boiling Fractions

Petroleum sources represent a virtually unlimited supply of polynuclear aromatics. The widely used catalytic cracking process produces, along with gasoline and gaseous hydrocarbons, a higher boiling fraction called cycle oil. This fraction is characterized by a high resistance to further catalytic cracking and contains a substantial amount of polynuclear aromatics. These aromatics are formed through a series of reactions involving removal of larger side chains, isomerization and dehydrogenation. The last reaction is in reality a hydrogen transfer reaction, wherein the hydrogen content of the lower boiling fraction is enriched at the expense of the higher boiling fraction. The usual composition pattern of the aromatic portion of cycle oil is extremely complex from the standpoint of the number of isomers; however, the actual composition by broad hydrocarbon class is much simpler in that the bulk of the material is represented by methylated polynuclear compounds. This is due to the fact that the less stable species are eliminated in catalytic cracking to give lower boiling compounds, leaving behind an equilibrated, highly stable structure. Typical components are mono- and dimethylnaphthalene followed by the methylated derivatives of tri- and tetra-ring condensed structures.

The removal of methyl groups followed by proper separation procedures represents a reasonable way of obtaining a variety of polynuclear compounds from petroleum sources. Such methods become particularly attractive when other sources cannot meet the demand. In the case of naphthalene, the coal-tar industry has dominated the market for many years, with an annual production of

500 million pounds. It should be remembered, however, that naphthalene, like ortho-xylene, is closely tied to the phthalic anhydride industry, with three-fourths of all naphthalene going to phthalic anhydride manufacture. Phthalic manufacturers have been hard-pressed at times to meet their phthalic demand because of a naphthalene shortage resulting from low steel production rates. In times of naphthalene shortage, ortho-xylene has been substituted in naphthalene-designed plants. This situation has also created a sizeable petroleum-naphthalene market. Thus, the hydro-dealkylation route is expected to become a major source of supply of this important chemical. Petroleum-naphthalene's high purity has provided an unexpected bonus in higher phthalic yields, making petroleum-naphthalene a much sought after chemical. Dependability of supply is another factor that has helped petroleum-naphthalene sales.

Despite ortho-xylene's invasion of the phthalic anhydride market, naphthalene consumption is expected to increase, reaching a figure of approximately one billion pounds by 1971, as illustrated in Figure 3. The naphthalene production and sales statistics are shown in Table 9.

Table 9 - CRUDE NAPHTHALENE STATISTICS
Millions of Pounds - (74 - 79°C)

Year	Production			Sales
	Coke-Oven	Tar Dist.	Total	
1950	99.7	188.8	288.5	206.7
1951	131.1	224.6	355.7	255.3
1952	106.9	215.6	322.5	209.8
1953	112.9	162.9	275.8	200.1
1954	100.1	195.1	295.2	224.2
1955	184.2	292.9	477.1	338.7
1956	177.3	314.2	491.5	289.0
1957	N.A.	N.A.	420.3	276.0
1958	N.A.	N.A.	345.1	212.6
1959	N.A.	N.A.	425.3	266.5
1960	N.A.	N.A.	517.0	310.3
1961	N.A.	N.A.	497.2	299.1

PRODUCTION AND SALES OF THE THREE GRADES AS OF 1960

	Millions of Pounds	
	Production	Sales
Solidifying at less than 74°C	24.7	26.0
Solidifying at 74°C to less than 76°C	21.5	10.2
Solidifying at 76°C to less than 79°C	470.9	274.1

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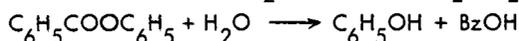
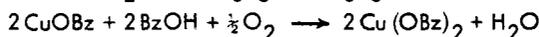
As pointed out above, other coal hydrocarbons can be produced from petroleum when the demand arises. The newly developed methods of separation, ⁽³⁾ based on differences in carbon-to-hydrogen ratios, can be used to provide hydrocarbon classes which can subsequently be demethylated and further purified by conventional means, such as distillation and crystallization.

D. Tar Acids

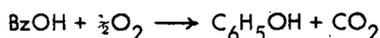
The tar acids are represented by phenol, cresols, cresylic acids and xylenols. The production of phenol from petroleum sources has grown very rapidly and five different processes are currently used:

1. Chlorobenzene Hydrolysis
2. Benzene Sulfonation
3. Cumene Peroxidation
4. Raschig Method
5. Two-Step Oxidation

Of these, the first three supply the bulk of the market. The cumene peroxidation process has been gaining in popularity and most of the new plants will employ this procedure. The two-step oxidation method is of considerable interest in that the starting material is toluene, which is oxidized to benzoic acid followed by the copper catalyzed oxidation to form phenylbenzoate and subsequent hydrolysis to produce phenol and benzoic acid. The reactions are believed to take place in the following manner:⁽⁴⁾



Overall Reaction:



The reaction can also be applied to the production of various cresols starting with toluic acids, as well as 2-naphthol using 1- or 2-naphthoic acids as raw materials. Synthetic phenol capacity in the U. S. is presently about 940 million pounds per year. If all announced plans for expansion and new plants materialize, capacity will be over 1.2 billion pounds by the end of 1963. Table 10 presents historical production and sales data.

Table 10 - PHENOL PRODUCTION AND SALES, 1950-1961

Year	Millions of Pounds							Total	Sales
	Production								
	Synthetic			Natural					
Cumene	Other Processes	Total	Coal Tar	Petroleum	Total				
1950	-	291.9	291.9	-	-	20.2	312.1	199.8	
1951	-	364.6	364.6	-	-	23.8	388.4	244.0	
1952	-	316.2	316.2	-	-	21.6	337.8	187.6	
1953	-	356.8	356.8	-	-	25.6	382.4	199.5	
1954	19.2	377.5	396.7	-	-	20.8	417.5	218.6	
1955	69.7	405.3	475.0	37.9	3.8	41.7	516.7	280.3	
1956	93.8	415.6	509.4	34.5	5.3	39.8	549.2	302.6	
1957	100.7	413.8	514.5	33.8	8.0	41.8	556.3	289.5	
1958	98.8	365.0	463.8	36.8	5.8	42.6	506.4	281.1	
1959	137.7	514.0	652.0	32.2	7.8	40.0	692.0	414.3	
1960	173.2	557.5	730.7	30.5	11.5	42.0	772.7	423.7	
1961	188.6	542.7	731.3	35.2	12.5	47.7	779.0	334.1	

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The market for phenol is dependent to a considerable extent upon the fortunes of phenolic resin manufacture, as indicated in Table 11. These resins account for roughly 60% of the phenol consumption. About one-third of all phenol produced is used as a chemical intermediate in the manufacture of alkyl phenols, bisphenol-A, polycarbonate resins and caprolactam. Phenol, in

the chlorinated form, is used in the manufacture of herbicides, the most important of which are 2,4-D and 2,4,5-T acid derivatives. The balance of phenol goes to the petroleum industry for solvent refining and additives and some for specialty products.

Table 11 - PHENOL END-USE PATTERN AS OF 1960

	<u>Percent of Total</u>
Phenolic Resins	58
Bisphenol-A	7
Caprolactam	7
Adipic Acid	6
Petroleum Solvent Refining	5
Pesticides	4
Alkylphenols	4
Miscellaneous (Aspirin, Polycarbonate Resins, Chlorinated, etc.)	9
	<u>100</u>

-0-

The actual production of phenol from 1950 through 1961 and estimated production through 1971 are shown in Figure 3. In 1961, 779 million pounds of phenol were produced with a predicted production of one billion pounds by 1965 and 1.4 billion pounds by 1971. If the present 85% ratio of production to capacity is maintained, 1,650 million pounds of phenol capacity will be needed at the beginning of the next decade.

E. Tar Bases

At the present time, petroleum sources are not utilized commercially for the production of tar bases, such as pyridine, picolines, pyrrole, quinoline, etc. The most important reason for not using petroleum sources is the absence of a substantial market. If such a market should develop, petroleum sources will undoubtedly be used. These sources should be considered as providing a large volume, low cost reactive hydrocarbon which can be converted into the desired tar bases. There are indications that various pyridines and indoles have attracted the attention of the petrochemical industry.^(5,6)

F. Miscellaneous Coal Chemicals

A number of sulfur and oxygen compounds derived from coal have presented interesting synthesis problems for the petrochemical industry. For example, considerable work has been done on the synthesis of thiophene using butadiene, butene and butane with sulfur and sulfur dioxide.^(7,8) Again, in this case, the raw materials derived from petroleum are available and can be used when a suitable market potential is developed.

-0-

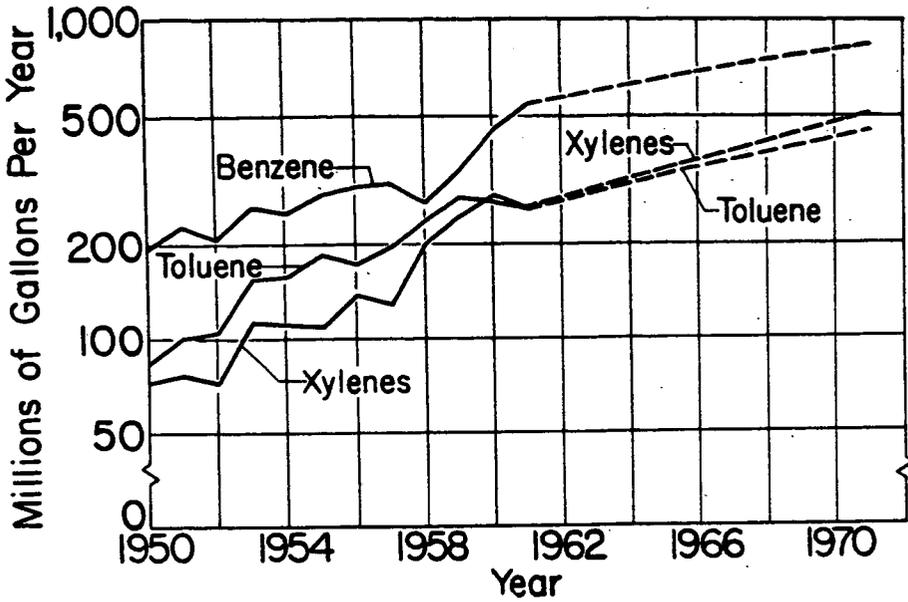
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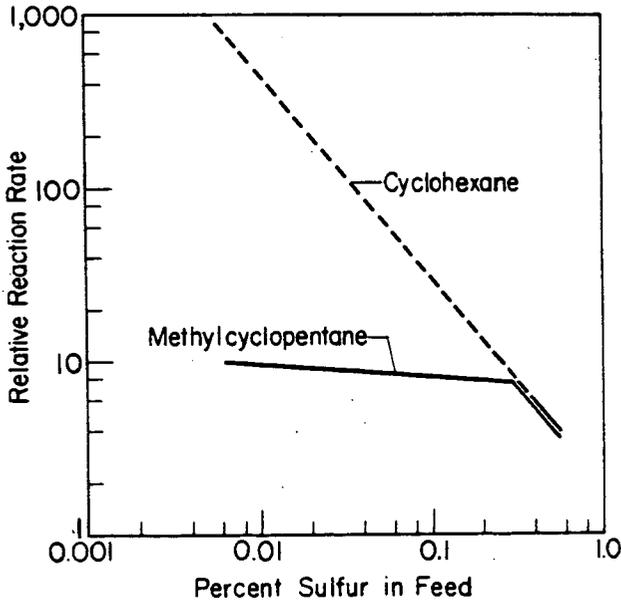
-9-

All statistical information has been gathered from the following:

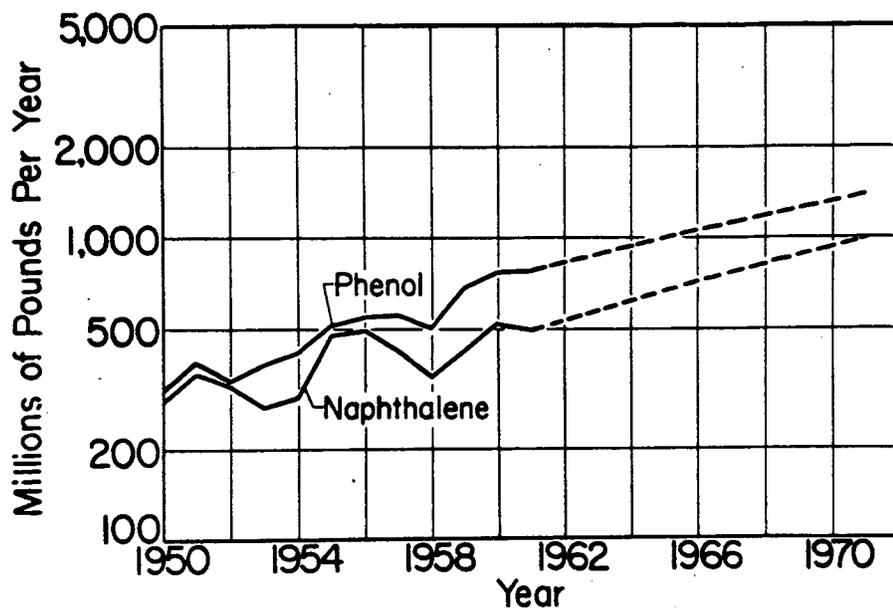
U. S. Tariff Commission
Stanford Research Institute
Oil Paint and Drug Reporter
Chemical Week
Chemical & Engineering News
World Petroleum
The Oil and Gas Journal



Benzene, Toluene and Xylenes Production
 1950-1961 Actual - 1962-1971 Estimated
 Figure 1



Effect of Sulfur on Conversion of Methylcyclopentane
 and Cyclohexane to Benzene
 Figure 2



Naphthalene and Phenol Production
1950-1961 Actual - 1962-1971 Estimated
Figure 3