

Aromatic Hydrocarbons

Manufacture and Technology

AROMATIC HYDROCARBONS

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Marshall Sittig

NOYES DATA CORPORATION

Park Ridge, New Jersey

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents relating to aromatic hydrocarbons. This includes two published patent applications.

This book is preceded by an introduction which is actually a comprehensive and penetrating market survey. This market survey is based on government reports and reflects the latest commercial data available.

The book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of the manufacture and technology of aromatic hydrocarbons.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas to research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You —

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses — many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
15. It is a creative source of ideas for those with imagination.

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INTRODUCTION

This volume presents an up-to-date summary of the production and use of aromatic hydrocarbons. The aromatics are key petrochemicals and their importance and versatility seems to increase with time.

Ironically, at the same time that aromatics are continuing in importance and indeed coal as a source of aromatics is receiving renewed attention, the available literature on the manufacture and use of aromatics is decreasing. The annual *Reviews of Benzole Technology* are no longer published by Benzole Producers, Ltd. in England. Journals like *Journal of the Institute of Petroleum* have also ceased publication so it is hoped that this volume will help to fill the gap in the technical literature.

Aromatics constitute one of the main classes of hydrocarbon building blocks—along with olefins and diolefins—on which the petroleum chemicals industry is based. Since World War I and the first coal tar dyes, benzene has been one of the backbones of the synthetic organic chemicals industry. The dominance of benzene as a raw material remains, but more and more benzene is being made from petroleum rather than coal—and the end uses extend far beyond mere dyestuffs into fibers, plastics, detergents, and a host of other products.

Toluene, once thought of largely as the basis for trinitrotoluene (TNT) is now finding expanding use as a solvent and as a chemical intermediate. The xylenes, once used almost exclusively in mixed forms as solvents, are now separated into the pure ortho, meta, and para isomers and used as chemical starting materials. Oxidation of the various xylenes to phthalic, isophthalic and terephthalic acids is typical of the new and growing uses for aromatics.

Naphthene-rich petroleum fractions are the most important sources of aromatic hydrocarbons. Aromatics are produced from these fractions by isomerization and dehydrogenation of the naphthenes, followed by separation of the aromatic hydrocarbon so produced plus whatever aromatic content which was present in the original petroleum fraction.


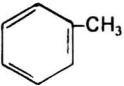
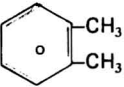
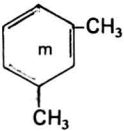

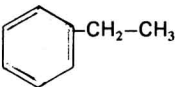
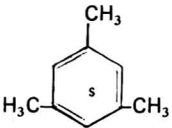
During World War I, the soaring demand for toluene as a raw material for TNT manufacture made separation from petroleum necessary, even though expensive processes had to be used. A narrow-cut virgin naphtha containing 25 to 35% toluene was thermally cracked, decomposing the nonaromatics to coke and light gases. The product liquid was acid treated to remove olefins and then redistilled to give nitration-grade toluene. Between 1920 and 1940, small amounts of mixed aromatics were obtained for solvent purposes by the extraction of petroleum fractions with sulfur dioxide.

At the beginning of World War II, the first commercial hydroforming unit was converted from motor gasoline production to toluene production. Under the wartime stimulus, seven other such units were placed in production and initiated the trend from coal to petroleum as the major source of aromatics. This trend was continued when benzene was produced commercially by dehydrogenation of cyclohexane starting about 1950.

Now, essentially all refineries rely primarily on the catalytic reforming of virgin naphthas and on the catalytic cracking of heavier oils to meet the volume and octane requirements of the motor gasoline market. Both the reforming and cracking processes produce large quantities of aromatic hydrocarbons and, thus, offer valuable sources of raw materials for the petrochemical industry. Steam cracking and coking processes also result in the production of some light aromatics; certain higher aromatics are produced in kerosene and lube oil processing operations. However, steam cracking and coking are of relatively little significance as producers of aromatics, and the higher aromatics are as yet of limited importance to the petrochemical industry.

The aromatics in catalytic reformates are thus by no means confined to benzene, toluene, and xylene, however. They include mesitylene and other C_9 aromatics and durene and other C_{10} aromatics. Table 1 shows the configurations of the various mononuclear aromatics which may occur in catalytic reformates. Various higher alkyl aromatics, from ethylbenzene to cumene to dodecylbenzene are also available by the alkylation of aromatics with olefins. Also, naphthalene is now available in quantity by the dealkylation of methyl-naphthalenes from petroleum.

TABLE 1: SOME MONONUCLEAR AROMATICS

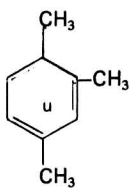
C_6H_6	Benzene	
C_7H_8	Toluene	
C_8H_{10}	Xylenes	  
	Ethylbenzene	
C_9H_{12}	Mesitylene	 1,3,5-

(continued)

TABLE 1: (continued)

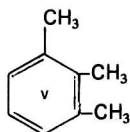
 C_9H_{12}

Pseudocumene



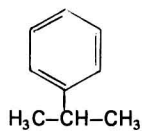
1,2,4-

Hemimellitene

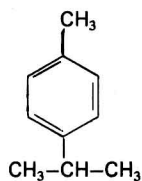


1,2,3-

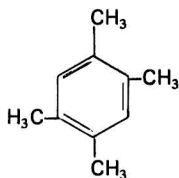
Cumene

 $C_{10}H_{14}$

Cymene

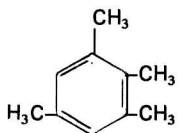


Durene



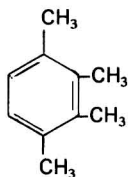
1,2,4,5-

Isodurene



1,2,3,5-

Prehnitene



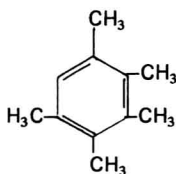
1,2,3,4-

(continued)

TABLE 1: (continued)

 $C_{11}H_{16}$

Pentamethylbenzene

 $C_{12}H_{18}$

Hexamethylbenzene

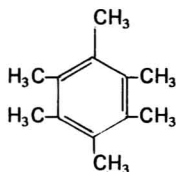


Table 2 shows some trends in aromatics production, consumption and prices as reported by the Office of Economic Impact, Federal Energy Administration in *Report to Congress on Petrochemicals*, Washington, D.C. (1975).

TABLE 2: PRIMARY AROMATICS—STATISTICAL SUMMARY*

Year	Capacity	Production	Imports	Exports	Apparent Consumption	Price
Benzene						
1971		1,076	77	43	1,110	\$0.20
1972		1,252	95	29	1,318	\$0.20
1973		1,458	52	30	1,487	\$0.27
1974	1,767	(+) 2-4%	(+) 25-30%	(+) 27-33%	(+) 2-5%	(+) 100-300%
1975	1,860	(+) 6-8%	(-) 8-14%	(+) 0-5%	(+) 5-8%	(-) 0-35%
Toluene						
1971		876	112	18	na	\$0.16
1972		916	149	26	na	\$0.17
1973		949	102	93	na	\$0.21
1974	1,013	(+) 10-15%	(-) 50-60%	(+) 6-8%	(+) 3-9%	(+) 100-150%
1975	1,080	(+) 2-7%	(-) 0-20%	(+) 0-1%	(+) 3-9%	(-) 0-35%
Xylene (mixed)						
1971		512	99	67	na	\$0.16
1972		736	84	128	na	\$0.17
1973		818	95	346	na	\$0.21
1974	1,162	(+) 5-9%	(-) 37-47%	(+) 25-46%	(+) 0-3%	(+) 90-180%
1975	1,162	(+) 9-13%	(-) 0-17%	(+) 0-17%	(+) 7-10%	(-) 0.30%

*Units: Capacity—millions of gallons.

All other—1971-73, millions of gallons or dollars per gallon.

—1974-75, percentage increase or decrease from previous year.

Source: Federal Energy Administration

BENZENE

Benzene, C_6H_6 , is a volatile, flammable, colorless, liquid hydrocarbon and possesses a characteristic aromatic odor. It is also called benzol in the trade but should not be confused with benzine (as gasoline is sometimes designated). The name benzene derives from the fact that it was first produced by the distillation of lime with benzoic acid. High-purity benzene has been available in quantity for a longer period of time than any other hydro-

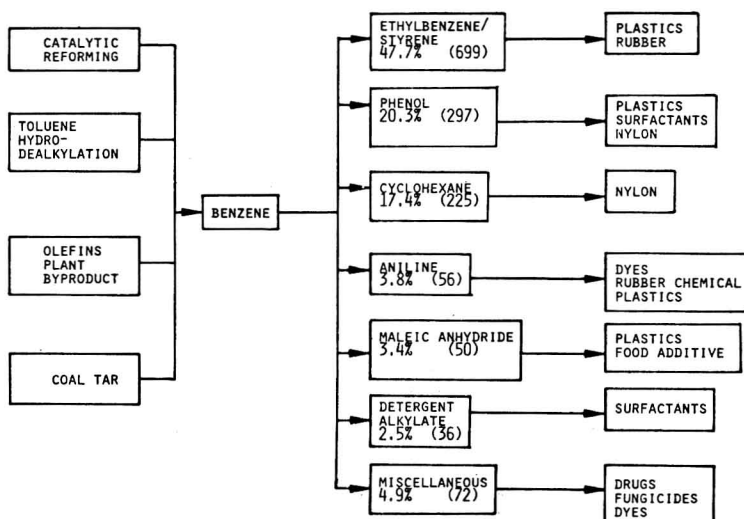
carbon. This combined with the fact that it undergoes a wide variety of reactions under mild conditions to give intermediates for many useful compounds accounts for its importance today. Benzene has long been produced by separation from the products of coal distillation and is still more dependent on coke ovens than on petroleum. This is because benzene constitutes perhaps 80% of coal tar while it may only be 20% of a catalytic reformate from which it is separated.

The major chemical uses for benzene today are as follows: styrene, nylon, aniline, maleic anhydride, BHC, 2,4-D, bisphenol, phenol, synthetic detergents, DDT, diphenyls, dichlorobenzenes, pentachlorophenol and aspirin. Benzene is available commercially in a research grade of about 99.95% purity, a pure grade of 99 mol percent minimum purity, and a technical grade of 95 mol percent minimum purity.

Benzene is one of the largest volume petrochemical (after ethylene and ammonia) with 1973 United States consumption of about 1,500 million gallons. Benzene is a basic raw material for the manufacture of dyes, drugs, plastics, rubber, synthetic fibers, detergents and pesticides. About 95% of benzene is currently made from petroleum with the remainder derived from coal tar. Figure 1 shows the sources and uses for benzene in 1973 from *Report to the Congress on Petrochemicals*, Washington, D.C., Federal Energy Administration (1975).

Benzene was first found by Michael Faraday in 1825 in a liquid by-product of the preparation of illuminating gas from whale oil. It was discovered in coal tar over a century ago, in 1845, and for nearly a century was predominantly of coal tar origin. Since World War II petroleum has come increasingly to the fore as a source of aromatics.

FIGURE 1: SOURCES AND USES OF BENZENE



Source: Federal Energy Administration

A substantial percentage of benzene is made from toluene. Benzene production had grown quite rapidly in the 1960s with production increasing 83% to 1,185 million gallons in 1969. Due to oversupply and depressed prices, most toluene hydroalkylation units were shut down; production decreased in 1970 and 1971 and production in 1972 was less than 6% above

the 1969 level. In 1972, U.S. industry had to rely on substantial imports and inventory reductions to meet demand. In 1973, although production increased 16% to 1,458 million gallons, supplies became very tight near the end of the year due to reduced imports and the depletion of inventories. Benzene exports were virtually unchanged from 1972. Early in 1974, the Federal Energy Administration raised the ceiling price of benzene so that an economic incentive was given to remove the product from the gasoline pool. Since 1972, producers have responded to the tight situation as shown in Table 3.

TABLE 3: BENZENE PRODUCTION

	Production Annual Rate (million gallons)	Percent Increase from 1972
1972	1,252	
1973, 1st half	1,401	11.9
1973, 2nd half	1,515	21.0
1974, 1st half	1,508	20.4

Source: Federal Energy Administration

At the end of 1973, producer inventories of benzene were at the very low level of slightly over eight days production. As of May 31, 1974, they had increased substantially to nearly eighteen days production, a more comfortable level but still somewhat under normal industry levels. Estimates on consumption of benzene compiled by the National Petroleum Refiners Association also indicate a recent trend towards slight excess of product availability (production plus imports less exports) to consumption.

It was expected that benzene production in 1974 would increase by 7%. An additional increase of 3% was expected for 1975. If demand for benzene remains sluggish and inventories continue to grow, some production could be curtailed. Basically, sufficient benzene should be available unless there is a sharp upsurge in demand even though the product should be basically tight for a number of years.

During 1974, prices of benzene continued to rise and are currently at the \$0.80 to \$0.90 per gallon level. On the other hand, spot prices which had reached \$2.50 to \$3.00 per gallon during the period of greatest tightness at the beginning of the year, have retreated to \$1.15 to \$1.25 per gallon or below. At present, world benzene prices have generally reached common levels and normal trade patterns in the product are again being established.

TOLUENE

Toluene, $C_6H_5CH_3$, is a liquid hydrocarbon—volatile, flammable, and colorless. It is the second member of the aromatic series beginning with benzene. Its odor is aromatic, like that of benzene, but milder and resembling the odor of balsam. Its name comes from the balsam of Tolu (in Colombia, South America). Toluene was first prepared in 1835 by the dry distillation of such a natural resin containing toluic acid esters. In commerce, toluene is also known as toluol. Historically, toluene was produced largely by separation from coal tar. Demands for toluene in wartime for TNT manufacture broke that pattern briefly even in World War I (when some toluene was separated from petroleum) and shattered it when the hydroforming process came into operation during World War II.

Thus, some years ago, there was a high demand for toluene which was used in the production of TNT. This led to the building of substantial facilities for its production. However, the advent of nuclear and fusion weaponry and the use of diesel oil-ammonium nitrate explosives has left toluene in substantial oversupply, since the only major uses of toluene are as a solvent and in the production of the following chemicals: diisocyanates, benzyl chloride, benzene, TNT, methylstyrene, saccharin, terephthalic acid. Since toluene, as well as benzene and xylene, have been used to a considerable extent in the preparation of nitro deriva-

tives, and since nitration processes are quite sensitive to feed impurities, the designation of nitration-grade aromatics has become very common. The specifications for nitration-grade benzene, toluene, and xylene are given in Table 4. In addition to the nitration grade of toluene designated by ASTM Specification D 841-50, there is an industrial grade designated by ASTM Specification D 842-50, whose purity is slightly lower, but quite adequate for solvent purposes. A 99.9% pure research grade is also commercially available.

TABLE 4: SPECIFICATIONS FOR NITRATION-GRADE AROMATICS

	Benzene ASTM-D 835-50	Toluene ASTM-D 841-50	Xylene ASTM-D 843-50
Specific gravity 15.56/15.56	0.8820-0.8860	0.8690-0.8730	0.8650-0.8700
Distillation range, initial to dry, °C	1.0	1.0	3.0
Boiling point, °C	80.1	110.6 ± 0.1	139.3***
Solidification point, °C minimum	4.85*	—	—
Saturates, percent by weight (maximum)	—	1.5**	4.0
Acid wash color (maximum)	2	2	2
Acidity	None	None	None
Sulfur	No H ₂ S or SO ₂	Same	Same
Copper corrosion	No coloration	Same	Same
Color	Not darker than 3 ppm K ₂ Cr ₂ O ₇ in H ₂ O	Same	Same

*Some users specify 5.0°C minimum.

**U.S. Army specifies 1.0% by volume.

***Minimum initial BP 137.2°C; maximum dry point 140.5°C.

Toluene is produced along with benzene and other aromatics by reforming. Toluene is recovered from the reformat by a relatively simple distillation operation, but if it is not separated it provides a valuable, high octane gasoline component. Because of its high octane rating, this alternate use of toluene in gasoline becomes more valuable with the restriction of tetraethyllead usage. Significant quantities of toluene are converted into benzene by dealkylation, but its major chemical uses are in the production of plastics, dyes, solvents, explosives, and a variety of specialty chemicals.

Production of toluene has grown at a rate of 7.5% per year over the last ten years to a level of 949 million gallons in 1973. Production through May of 1974 was at an annual rate of 1,235 million gallons, 32% ahead of 1973. During 1973 and early 1974 inventories rose steadily to a level of 90 million gallons as of May 31, 1974, a 53% increase from December 31, 1972, and equivalent to a 27 day supply at then current production rates.

The recent increase in production which more than offset the reversal in import-export balance, illustrates the relative ease with which toluene can be diverted from fuel to chemical use as economics and other factors dictate. In contrast to the severe shortages which existed at the beginning of the year, the supply of toluene should be adequate for the immediate future period with prices stabilizing in the range of 45¢ per gallon.

C₈ AROMATICS

The xylenes, C₆H₄(CH₃)₂ are the third member of the aromatic series of hydrocarbons, the first two being benzene and toluene. Again, they are colorless, volatile, flammable liquids with pleasant aromatic odors. Crude xylene was first prepared in 1850 by the destructive distillation of wood tar and hence received the name xylene from the Greek xylos for wood and the -ene suffix meaning oily.

In the case of xylene, since there are two methyl groups, we have for the first time in the benzene series the problem of position isomerism. When the two methyl groups are in adjacent positions, we have o-xylene; when they are in a 1,3- relationship, we have m-xylene and when they are at opposite poles of the benzene ring in a 1,4- position, we have p-xylene. This o-xylene, m-xylene, p-xylene designation is part of the basic nomenclature of all aromatic chemistry, and is used to designate halogen, sulfuric acid and other derivatives as well as alkyl derivatives of benzene, in the case of the xylenes. Each of the C₈ aromatic hydrocarbons is produced commercially in high purity by separation from catalytic reformates. Table 5 shows the boiling and freezing points of these materials and their percentages in a typical reformate.

TABLE 5: COMPOSITION OF C₈ AROMATICS IN REFORMATE

Compound	Boiling Point (°F)	Freezing Point (°F)	Weight Percent of C ₈ Aromatics
Ethylbenzene	277	-139	21.2
p-Xylene	281	+56	18.3
m-Xylene	282	-54	40.4
o-Xylene	292	-13	20.1
			100.0

Commercially, nitration-grade xylene having a 3°C boiling range is available, as is a so-called ten degree xylene. The trend is to purer mixed xylenes and to the pure separated xylene isomers, however.

Of the various aromatics in petroleum, the xylenes have a huge future production potential increase—greater than the potential percentage increase for either benzene or toluene. Like toluene, mixed xylenes are separated from aromatic-rich refinery streams and from pyrolysis gasoline recovered during the production of olefins. Minor amounts are produced from coal tar. Only a small percentage of xylenes produced in refineries is diverted to petrochemical use. United States production of mixed xylenes for chemical use has grown at a rate of 10.6% per year over the last ten years.

Production of o-xylene has increased by an average of 13% per year over the last ten years to 1.1 to 1.2 billion pounds per year in 1973 and early 1974. Imports are not reported separately and exports have dropped steadily as a percent of production from 57% in 1968 to 17% in 1974. Inventories decreased slightly in 1973 but in mid-1974 climbed to a level of 128 million pounds (39 day supply), almost 50% above the level of December 31, 1972. Installed capacity on January 1, 1974 was 1,588 million pounds so that operation is estimated to be at about 75% of capacity. Adequate supplies should thus be a function of feedstocks availability and the degree of use in gasoline.

p-Xylene production has shown an average growth of 24% per year over the last ten years, 11% per year over the last five years, and 5% for 1973 over 1972. However, production through mid-1974 was 10% ahead of the corresponding period in 1973. Imports of p-xylene are not separately reported and exports have decreased steadily from 14% of production in 1971 (the first year in which exports were identified) to 1.5% in 1974.

p-Xylene production capacity, reported to be 2,775 million pounds on January 1, 1974, operated at 98% capacity in the March-May 1974 period. Despite the high level of operation, inventories which dropped by 10% during 1973 increased slightly in 1974 to a 24 day supply in mid-1974. With additional capacity expected on stream, this situation should be relieved and the outlook for p-xylene improved.

o-Xylene

Of the various C₈ aromatics, o-xylene is easiest to separate and it was first produced commercially in 1945. It is usually separated by fractional distillation.