Alkylbenzenes in the C_8 Fraction From Five Different Catalytic Petroleum Refining Processes[1][2][3]

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This report gives the results of the analysis, by measurements of freezing points of appropriate mixtures, supplemented by analytical distillation, of the four individual C_8 alkylbenzenes (ethylbenzene, o-xylene, m-xylene, and p-xylene) occurring in the product from the following five different catalytic petroleum refining processes: (1) Hydroforming, (2) Two-pass Fixed Bed, (3) Three-pass Fixed Bed, (4) Low-temperature Fluid, and (5) High-temperature Fluid. The data indicate that the relative amounts by volume of the four C_8 alkylbenzenes are not greatly different in the five different products being, on the average, as follows: ethylbenzene, 12; o-xylene, 21; m-xylene, 48; p-xylene, 19. These amounts correspond substantially to those called for in chemical thermodynamic equilibrium for the operating temperatures involved.

I. Introduction

As part of its war research program, the American Petroleum Institute Research Project 6 at the National Bureau of Standards was requested to analyze the individual alkylbenzenes in the C_8 fraction from five different catalytic petroleum refining processes. The investigation was completed early in 1943, and the results on the composition were correlated, by appropriate other laboratories, with manufacturing conditions and with engine performance, to improve the utility of these materials as components for aviation fuel. This report gives the results of the analysis of the amounts of ethylbenzene, o-xylene, m-xylene, and p-xylene in the product from these five different catalytic petroleum refining processes.

II. Materials Analyzed

The five lots of material that were analyzed in this investigation are listed in table 1, which gives the name of the process that produced the material, the name of the company that supplied the sample, the approximate temperature and pressure in the reaction zone, and the charging stock.

The process labeled hydroforming is one in which material of the gasoline range is reformed, in the presence of a catalyst and hydrogen, to give material of nearly the same boiling range but of appreciably higher aromatic content.

The process labeled two-pass fixed bed is a catalytic-cracking one of Houdry design, in which material of the gas oil or heavier distillate range is cracked in the presence of a catalyst in a fixed bed, with the gasoline fraction from the first operation repassed through a similar operation.

The process labeled Three-pass Fixed Bed is also a catalytic cracking process of Houdry design and is operated similarly. The charging stock for this process was heavy naphtha accumulated from the two-pass fixed bed process.

The process labeled Low-temperature Fluid and the one labeled High-temperature Fluid are catalytic cracking processes in which a fluid catalyst is moved continuously through the reaction zone, with the catalyst being reactivated in continuous flow through a separate chamber. The charging stock here is kerosine or gas oil.

All of the foregoing processes have been described many times in technical articles in the petroleum journals, and readers will readily find them under the names given above or the follow-

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[1] This investigation was performed as part of the work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the Analysis, Purification, and Properties of Hydrocarbons.

[2] This paper is a revision of a restricted report of the American Petroleum Institute Research Project 6 at the National Bureau of Standards issued under date of July 31, 1943, with the title "Analysis of the Aromatic Hydrocarbons in the C_8 Fractions of High Aromatic Stocks from Five Different Plant Processes."

[3] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the meeting at Atlantic City, N. J., in April 1947.

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TABLE 1. *Information concerning the samples analyzed*

Catalytic petroleum refining process	Supplier	Temperature in reaction zone (approximate)			Pressure in reaction zone		Charging stock
		°F	°C	°K	lb/in.² (gage)	atm	
Hydroforming..................	Humble Oil and Refining Co., Houston, Tex.	925	496	769	215	15. 6	Selected naphtha.
Two-pass fixed bed.................	Sun Oil Co., Marcus Hook, Pa.........	850	454	727	50	4. 4	Gas oil plus heavy distillate from Mid-continent and Gulf coast crudes.
Three-pass fixed bed.	Socony-Vacuum Oil Co., Paulsboro, N. J.	875	468	741	33	3. 2	Heavy naphtha from two-pass fixed bed catalytic process.
Low-temperature fluid.	Standard Oil Development Co., Elizabeth, N. J.	800	427	700	....	....	Mirando kerosine.
High-temperature fluid............	Standard Oil Development Co., Elizabeth, N.J.	975	524	797	....	....	Southwest Louisiana gas oil.

ing: Hydroforming petroleum refining process; Houdry catalytic cracking process; fluid catalytic cracking process.

Each of the five materials analyzed may be described as that part of the product of the given plant process containing all of the four C_8 aromatic hydrocarbons, which have normal boiling points as follows: Ethylbenzene, 136.19° C; o-xylene, 144.42° C; m-xylene, 139.10° C; p-xylene, 138.35° C. Each sample was prepared by the supplier by distillation of the whole product from the given plant process. A small amount of toluene (at 110.62° C) and a small amount of isopropylbenzene (at 152.40° C) and higher C_9 alkylbenzenes were included in the material blended to form the sample for analysis in the present investigation, in order to insure the presence in the given sample of substantially all of the C_8 aromatic hydrocarbons from the original stock. Because some of the samples were prepared so as to include more C_7 and C_9 aromatics than others, the relative amounts of the C_7 and C_9 aromatics to the C_8 aromatics have no significance. Likewise, the aromatic content of the original material as submitted for analysis would depend upon how much of the C_7 and C_9 hydrocarbons (aromatics plus paraffins and naphthenes) was included.

The data that have an important significance are the relative amounts of the four C_8 alkylbenzenes in the five samples.

III. Method of Analysis

The method of analysis developed for this investigation is as follows:

(a) A sample of the material is subjected to an analytical determination of the aromatic content by adsorption [1][5]. The amount of material processed in the adsorption experiment is selected so as to produce not less than 15 ml of a portion that contains all the aromatics, with only a small amount or none of the nonaromatic hydrocarbons. The results of the analytical adsorption experiment on the sample from the Hydroforming process are shown in figure 1, and the corresponding results on the sample from the High-temperature Fluid process are shown [6] in figure 2.

(b) Using the aromatic portion obtained as described in (a), experiments are made to determine the lowering of the freezing point of samples of "pure" ethylbenzene, p-xylene, m-xylene, and o-xylene, respectively, produced by the addition of small measured amounts (in the range 5 to 7 percent) of the given unknowns to the given "pure" compounds. Each such measurement of the lowering of the freezing point produces a value of the amount of the given hydrocarbon in the unknown mixture. This procedure requires that the molecular weight of the unknown be known. If it is not known, a determination of the molecular weight may be made by measuring the lowering of the freezing point produced by the addition of a small measured amount of the given unknown to "pure" benzene (provided benzene is known not to be a component of the unknown). This method of determining individual hydrocarbons in mixtures of hydrocarbons by measurement of freezing points is described in detail in reference [2]. The "unknown" sample for which complete data are

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[5] Figures in brackets indicate the literature references at the end of this paper.

[6] If, as may be probable, there is no significant difference between the relative amounts of the four C_8 aromatic hydrocarbons at the front and back ends of the aromatic plateau from the adsorption experiment, then the aromatic portion may be taken substantially free of nonaromatic compounds.
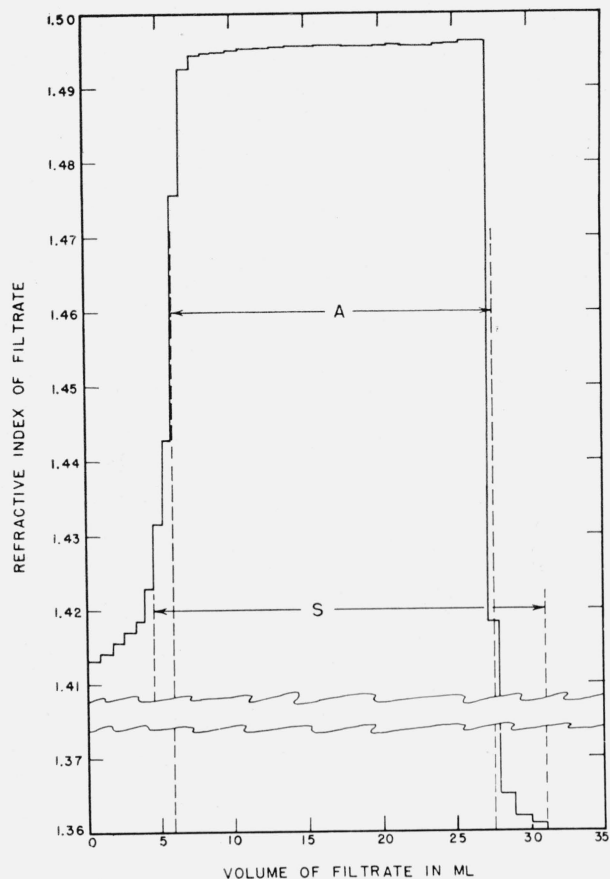
FIGURE 1.—*Results of the analytical adsorption experiment on the sample from the Hydroforming process.*

The refractive index of the filtrate is given as a function of its volume. The volume represented by A measures the aromatic content of the material. The volume constituted by S shows the material that is to be mixed to constitute the sample of aromatic hydrocarbons (after the ethyl alcohol at the tail end is removed by washing).

given in table 1 of [2] is the Two-pass Fixed-Bed sample listed in table 1 of this report.

Although the foregoing represents the procedure finally selected as being the best for analyses of the kind described, actually many more observations of other kinds were made on the materials in order to work out the simplest and most reliable method of analysis. For example, in order to obtain larger quantities of the aromatic portion than are recommended above, the separation of the nonaromatic hydrocarbons from the aromatic hydrocarbons was also performed by a method previously described [3]. This method involves separation of the nonaromatic hydrocarbons from the aromatic hydrocarbons in the adsorption column by displacement with pentane, the subsequent removal of the hydrocarbons from the adsorption column with methanol

and the removal from the aromatic hydrocarbons of methanol by extraction with water and of pentane by distillation. The use of this procedure is also described in reference [5].

The aromatic content was determined not only by the simple adsorption procedure described under (a) above, but also by comparison of the refractive index of the original material with the refractive index of mixtures made by remixing known amounts of the aromatic portion and the nonaromatic portion, obtained as described in the preceding paragraph.
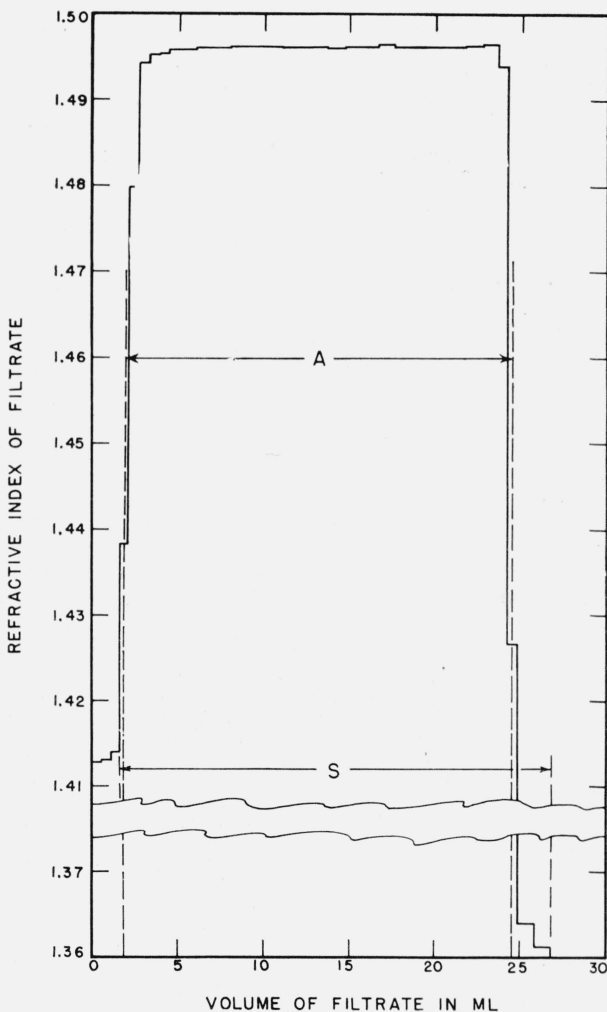

FIGURE 2.—*Results of the analytical adsorption experiment on the sample from the High-temperature Fluid catalytic cracking process.*

The refractive index of the filtrate is given as a function of its volume. The volume represented by A measures the aromatic content of the material. The volume constituted by S shows the material that is to be mixed to constitute the sample of aromatic hydrocarbons (after the ethyl alcohol at the tail end is removed by washing).

Alkylbenzenes in the C$_8$ Fraction

The amounts of toluene, of the sum of ethyl-benzene plus p-xylene plus m-xylene, of o-xylene, and of the C_9 aromatics in the aromatic portion, were determined by an analytical distillation of about 180 ml of the aromatic portion at a high reflux ratio in a rectifying column of high efficiency and low hold-up, using n-decane or diethyl-benzene as a "chaser". These distillations were performed, under the supervision of C. B. Willingham, in distilling columns identical with still No. 2 described in table 1 of reference [4]. The results of these distillations (except for the relative amounts of the components) were similar to the results presented in figures 8 to 14, inclusive, of reference [6].

The molecular weights of the given aromatic portions were calculated from the relative amounts of the C_7, C_8, and C_9 aromatic hydrocarbons as determined from the distillation and also from measurements of the lowering of freezing point in benzene, as described in (b) above.

IV. Results

The values of the bromine number, and the content of olefins, aromatics, and paraffins plus naphthenes, for the materials as received, are given in table 2.

TABLE 2.—*Content of olefin, aromatic, and paraffin plus naphthene hydrocarbons in the samples as received*

Sample	Bromine number [a]	Content of olefins [b]	Content of aromatics [c]	Content of paraffins plus naph-thenes (by difference)
	g/100 g	*Percentage by vol.*	*Percentage by vol.*	*Percentage by vol.*
Hydroforming	0. 50	0. 4±0. 1	(I) 91.8±0.5	8. 0±0. 4
			(II) 91.3± .5	
			Mean 91.6± .4	
Two-pass fixed bed	1. 59	1.4± .2	(I) 55.2± .5	43. 3± . 4
			(II) 55.5± .5	
			Mean 55.3± .4	
Three-pass fixed bed	1. 15	1.0± .2	(I) 85.3± .5	13. 2± . 4
			(II) 86.3± .5	
			Mean 85.8± .4	
Low-temperature fluid	3. 84	3.5± .3	(I) 77.2±1.0	18. 4± . 8
			(II) 79.0±1.0	
			Mean 78.1± .7	
High-temperature fluid.	15. 06	13.5±1.0	(I) 78.4±1.0	7. 1±1. 2
			(II) 80.4±1.0	
			Mean 79.4± .7	

[a] Determined by R. C. Hardy, Section 3.5, National Bureau of Standards.
[b] Calculated assuming the olefins to be C_9H_{18} and the ratio of the density of the aromatics to the olefins to be 1.18.
[c] Determined independently in two ways, (I) giving values obtained by the simple adsorption experiments (performed by B. J. Mair) described in this report, and (II) giving values obtained by refractive index measurements on the original material and appropriate mixtures of the aromatic and non-aromatic portions of the original material.

The amounts of C_7, C_8, and C_9 aromatic hydro-carbons in the aromatic portion of each material, as determined from the analytical distillations, are given in table 3. This table also gives values for the molecular weight of the aromatic portion as calculated from the data from the analytical dis-tillation and as determined from measurements of the lowering of the freezing point in benzene.

In table 4 are given values of the amounts of each C_8 aromatic hydrocarbon determined to be in the aromatic portion by means of measurements of freezing points, and the sum of the amounts of the four C_8 aromatic hydrocarbons as so determined. It is interesting to note the good accord between the values given in the last column of table 4 with the corresponding values given in the third column of table 3.

In table 5 is given a comparison of the content of

TABLE 3.—*Amounts of the C_7, C_8, and C_9 aromatic hydro-carbons in the aromatic portion, and the molecular weight of the aromatic portion*

Sample	Amounts (% by volume) of aromatic hydrocarbons—			Molecular weight of the ar-omatic portion[a]	
	C_7	C_8	C_9	I	II
				g/mole	*g/mole*
Hydroforming	0.7±0.3	94.4±0.5	4.9±0.5	106.65	107.56
Two-pass fixed bed	3.3± .5	85.0± .5	11.7± .5	107.06	107.31
Three-pass fixed bed	2.9± .5	94.2± .5	2.9± .5	106.05	105.18
Low-temperature fluid	0.5± .3	97.3± .5	2.2± .5	106.34	105.90
High-temperature fluid	0.5± .3	97.9± .5	1.6± .5	106.27	106.04

[a] Determined independently in two ways, column I giving values calcu-lated from the distillation data, and column II giving values determined from the lowering of the freezing point in benzene, as described in part III of refer-ence [3]. The molecular weight of a C_8 aromatic is 106.16.

TABLE 4.—*Amounts of the four C_8 alkylbenzenes in the aromatic portion, as determined from freezing-point measurements*

Sample	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene	Total of C_8 aro-matics
	Percentage by volume [a]				
Hydroforming	11.2±1.2	17.2±1.2	45.1±1.2	23.5±1.2	97.0±2.4
Two-pass fixed bed	11.4±1.2	16.4±1.2	41.4±1.2	16.9±1.2	86.1±2.4
Three-pass fixed bed	8.0±1.2	18.9±1.2	48.5±1.2	17.6±1.2	93.0±2.4
Low-temperature fluid	12.9±1.2	17.5±1.2	45.7±1.2	24.3±1.2	100.4±2.4
High-temperature fluid	12.4±1.2	19.4±1.2	48.6±1.2	17.7±1.2	98.1±2.4

[a] The uncertainty of ±1.2 percent assigned to the amount of each C_8 aro-matic hydrocarbon in the aromatic portion is the resultant of an estimated uncertainty of ±1.0 percent in the determination of the lowering of the freezing point and of ±0.5 percent in the determination of the molecular weight of the unknown mixture.

o-xylene in the five materials as determined by measurements of freezing points and as determined from the data of the analytical distillation.

TABLE 5.—*Comparison of the content of o-xylene in the aromatic portion as determined (I) from the measurements of freezing points and (II) from the analytical distillation*

Sample	Amount of o-xylene	
	I	II
	Percentage by vol.	Percentage by vol.
Hydroforming	23.5±1.2	22.6±1.0
Two-pass fixed bed	16.9±1.2	17.6±1.0
Three-pass fixed bed	17.6±1.2	18.0±1.0
Low-temperature fluid	24.3±1.2	23.8±1.0
High-temperature fluid	17.7±1.2	17.6±1.0

TABLE 6.—*Relative amounts of the four C_8 alkylbenzenes as determined from freezing-point measurements* [a]

Sample	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene	Total
	Percentage by volume				
Hydroforming	11.6±1.0	17.7±1.0	46.5±1.0	24.2±1.0	100
Two-pass fixed bed	13.2±1.0	19.1±1.0	48.1±1.0	19.6±1.0	100
Three-pass fixed bed	8.6±1.0	20.3±1.0	52.2±1.0	18.9±1.0	100
Low-temperature fluid	12.9±1.0	17.4±1.0	45.5±1.6	24.2±1.0	100
High-temperature fluid	12.6±1.0	19.8±1.0	49.6±1.0	18.0±1.0	100
Mean value	11.8	18.8	48.4	21.0	_____
Average difference between the mean and the individual values	±1.3	±1.0	±2.0	±2.6	_____
Maximum difference between the mean and the individual values	−3.2	+1.5	+3.8	+3.2	_____

[a] The values given in this table are those from table 4 recalculated to make the sum of the amounts of the four C_8 aromatics equal to 100 percent. The assigned uncertainty arises only from the determination of the lowering of the freezing point, since an uncertainty in the molecular weight of the unknown mixture of aromatic hydrocarbons does not affect the relative amounts of the four C_8 aromatic hydrocarbons.

In table 6 are given values for the relative amounts of the C_8 aromatic hydrocarbons in each of the five different materials, as determined from measurements of the lowering of the freezing point. At the bottom of table 6 are also given for each compound, for the five samples, (a) the mean value, (b) the average difference between the mean and the individual values, and (c) the maximum difference between the mean and the individual values.

V. Discussion

In connection with the results obtained in this investigation, the following conclusions may be drawn:

(a) The relative amounts of the four C_8 alkylbenzenes are nearly the same in the product from all five of the catalytic petroleum refining processes. This is clearly shown by the results in table 6, which gives the following for the mean value and for the average difference between the mean and the individual values: Ethylbenzene, 11.8, ±1.3; p-xylene, 18.8, ±1.0; m-xylene, 48.4, ±2.0; o-xylene, 21.0, ±2.6.

(b) The relative amounts of the four alkylbenzenes are, on the average, within the estimated limits of uncertainty, equal to the relative amounts that would be expected at thermodynamic equilibrium at the temperature at which the material was produced. This is clearly shown by the results given in table 7, which gives for each process the temperature, the actual amount, and calculated equilibrium amount for each of the four C_8 alkylbenzenes. The calculated values for thermodynamic equilibrium given in table 7 are taken from reference [7].

TABLE 7.—*Comparison of the actual composition with that calculated for thermodynamic equilibrium at the given temperature (Actual values from table 6 of this report; calculated values from reference [7])*

Sample	Tempera-ture	Relative Amounts of the Four C_8 Alkylbenzenes							
		Ethylbenzene		p-Xylene		m-Xylene		o-Xylene	
		Actual	Calculated	Actual	Calculated	Actual	Calculated	Actual	Calculated
	°K								
Hydroforming	769	11.6±1.0	10.0±1.5	17.7±1.0	20.9±3.5	46.5±1.0	46.4±5.0	24.2±1.0	22.7±3.5
Two-pass fixed bed	727	13.2±1.0	9.0±1.5	19.1±1.0	21.2±3.5	48.1±1.0	47.3±5.0	19.6±1.0	22.5±3.5
Three-pass fixed bed	741	8.6±1.0	9.4±1.5	20.3±1.0	21.1±3.5	52.2±1.0	46.9±5.0	18.9±1.0	22.6±3.5
Low-temperature fluid	700	12.9±1.0	8.3±1.5	17.4±1.0	21.5±3.5	45.5±1.0	47.8±5.0	24.2±1.0	22.4±3.5
High-temperature fluid	797	12.6±1.0	10.7±1.5	19.8±1.0	20.6±3.5	49.6±1.0	45.9±5.0	18.0±1.0	22.8±3.5

VI. References

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