Seventeen Aromatic Hydrocarbons Separated from the 180° to 200° C. Fraction of Petroleum

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As PART of the continuing work of the American Petroleum Institute Research Project 6 on the composition of petroleum, analysis has been completed for the C_{10} alkylbenzenes and C_{10} alkylindans in the aromatic portion normally boiling between 180° and 200° C. The details of the analysis of the aromatic hydrocarbons in the adjacent lower boiling fraction of this petroleum have been given (2).

The seventeen compounds, and their amounts, in order of decreasing percentage by volume of the petroleum are: 1,2,3,5-tetramethylbenzene, 0.12; 1-methyl-3-propylbenzene, 0.066; 1,3-dimethyl-5-ethylbenzene, 0.063; 1,2-dimethyl-4-ethylbenzene, 0.057; 1,2,4,5-tetramethylbenzene, 0.052; 1,3-dimethyl-4-ethylbenzene, 0.050; 1-methyl-2-propylbenzene, 0.046; 1,4-dimethyl-2-ethylbenzene, 0.041; 1,2-dimethyl-3-ethylbenzene, 0.036; 1,3-diethylbenzene, 0.033; 1-methyl-4-propylbenzene, 0.027; *n*-butylbenzene, 0.026; 1-methylindan plus 2-methylindan, 0.027; 1,3-dimethyl-2-ethylbenzene, 0.014; 1,4-diethylbenzene, 0.007; 1,2-diethylbenzene, 0.005. The remainder of this fraction consists of unidentified C_{11} alkylbenzenes and C_{11} alkylindans, which amount to 0.15 and 0.015% by volume, respectively, of the petroleum.

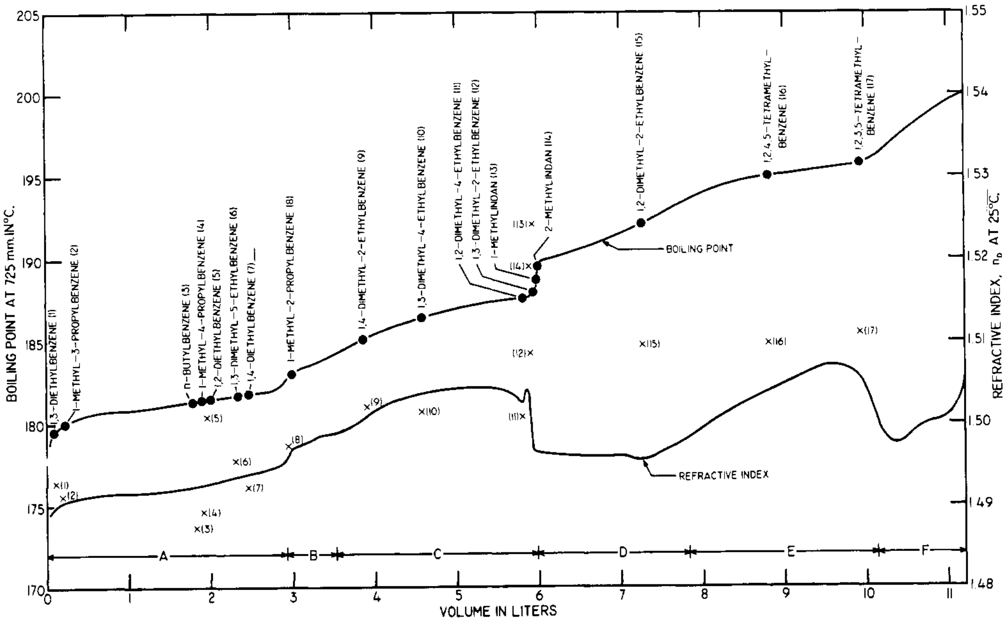


Figure 1. Results of distillation of the 180° to 200° C. aromatic fraction of petroleum

The circles and crosses give, respectively, the boiling points and refractive indices of the compounds isolated.

Azeotropic Distillation Results

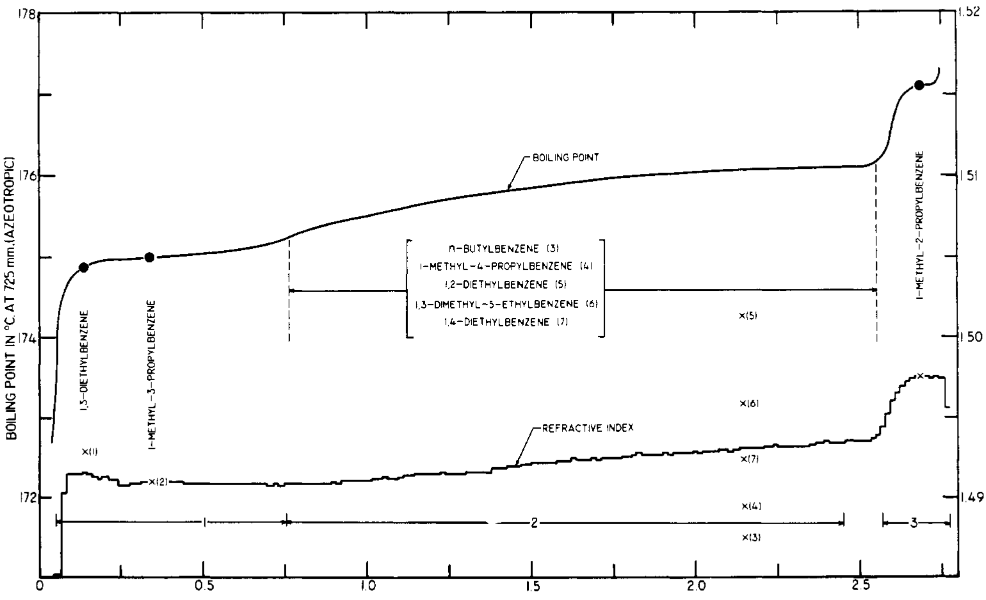


Figure 2. Portion A

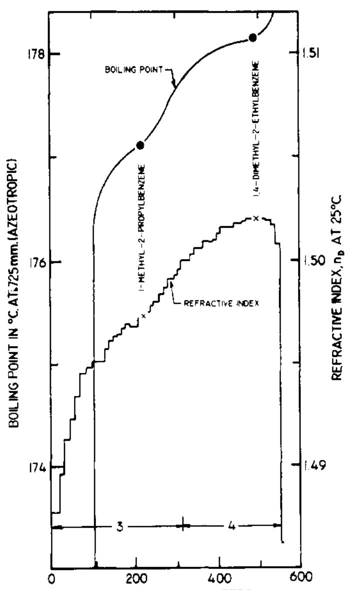


Figure 3. Portion B

Azeotropic Distillation Results

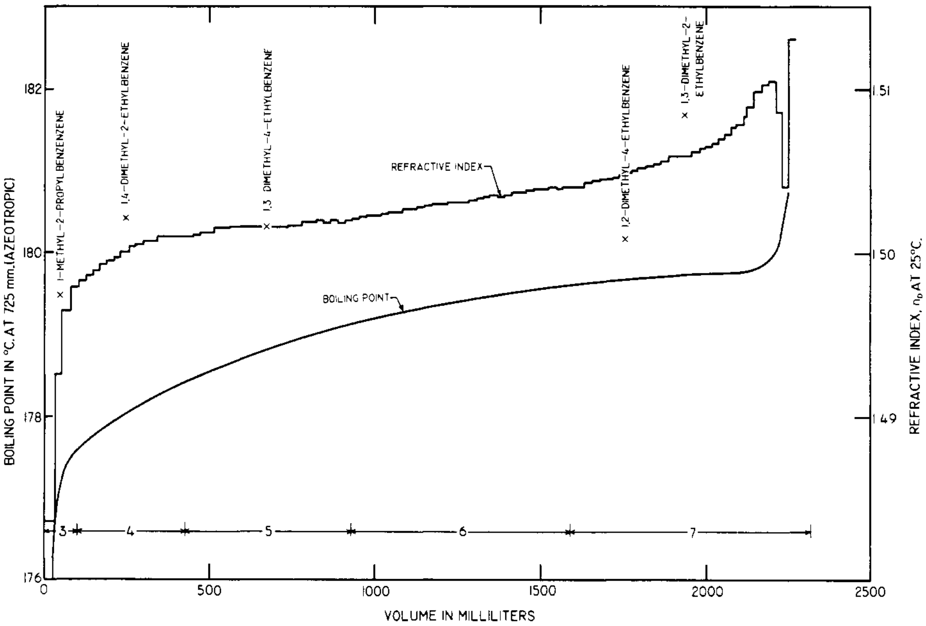


Figure 4. Portion C

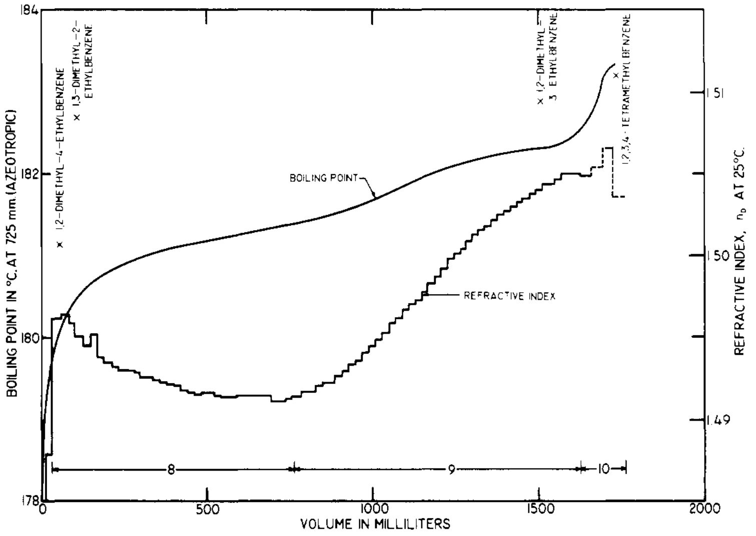


Figure 5. Portion D

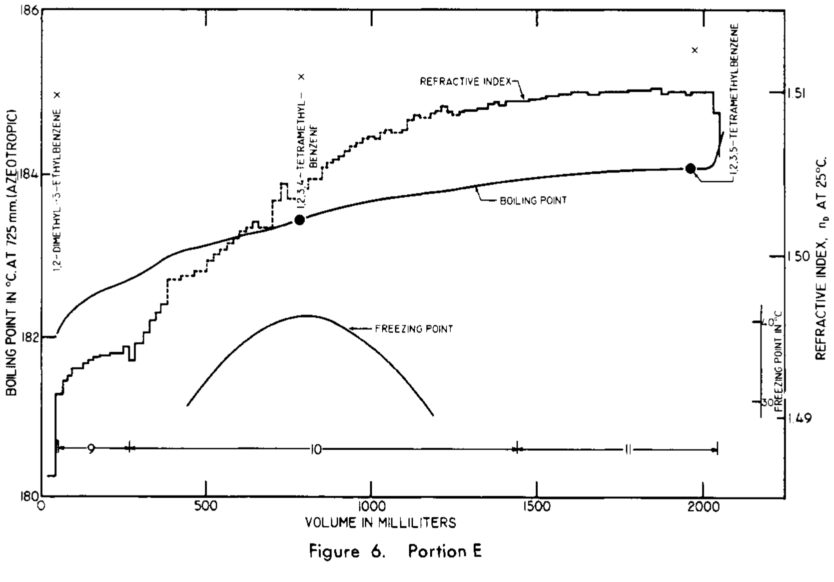


Figure 6. Portion E

MATERIAL ANALYZED

The aromatic material was separated by azeotropic distillation and adsorption from the original petroleum boiling in the range from 177° to 200° C. (*1*). A total of 13.0 liters constituting 16.1% of the entire distillate, 177° to 200° C., representing 1.0% of the total crude petroleum, was obtained. Part of this material boiled outside the range covered by the present investigation. The portion actually distilling within the selected range, 180° to 200° C., represented approximately 0.83% by volume of the petroleum.

INITIAL PROCESSING

The aromatic material from the original distillate, 177° to 200° C., was distilled twice in columns of high separating power (*3*). The results of the second distillations are given in Figure 1. The distillate was divided into portions A, B, C, D, E, and F. These portions were processed separately by azeotropic distillation with diethylene glycol monomethyl ether (methyl Carbitol). Figures 2 to 7 give the results of these distillations. The distillate from this operation was blended, as shown, to give portions 1 to 11, which were processed as follows: portions 1 and 2 by absorption; portion 3 by azeotropic distillation; portions 4 to 6 by regular distillation at 217 mm. of mercury; portion 7 by regular distillation at 30 mm. of mercury; portions 8, 9, and 11 by regular distillation at 760 mm. of mercury; and portion 10 by crystallization to remove the bulk of the 1,2,4,5-tetramethylbenzene, followed by regular distillation of the mother liquors (labeled portion 10A). In addition to material which resulted from the distillation of portions E and F (Figures 6 and 7), portion 11 contained a small part of the distillate from portion 10A (Figure 15). The results of the distillations of portions 3, 4, 5, 6, 7, 8, 9, 10*A*, and 11 are shown in Figures 8, 9, 10, 11, 12, 13, 14, 15, and 16 respectively.

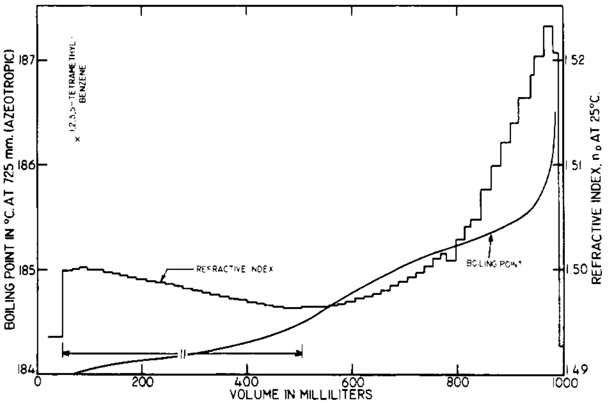


Figure 7. Portion F

Distillation Results

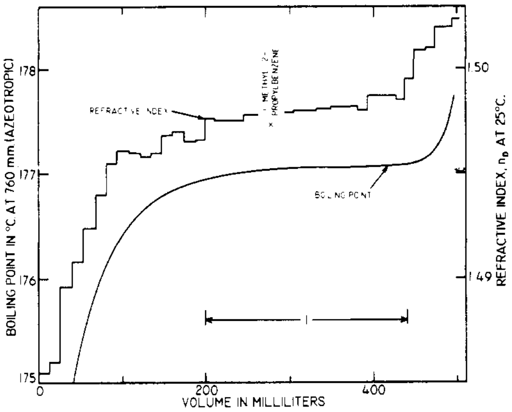


Figure 8. Portion 3 (Figures 2,3, and 4)

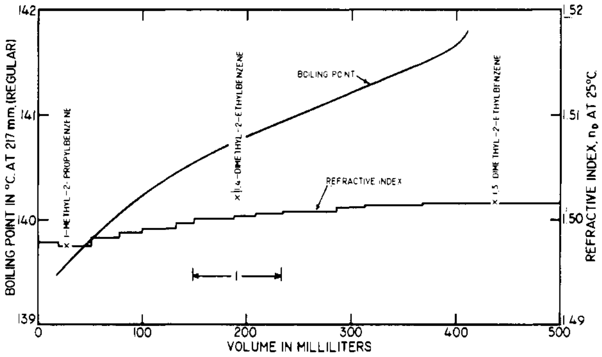


Figure 9. Portion 4 (Figures 3 and 4)

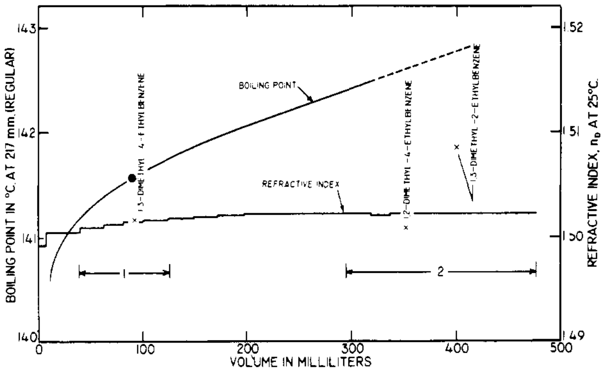


Figure 10. Portion 5 (Figure 4)

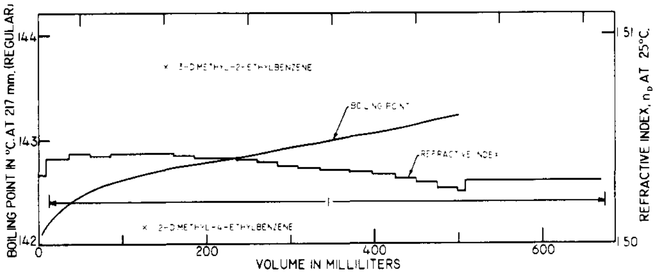


Figure 11. Portion 6 (Figure 4)

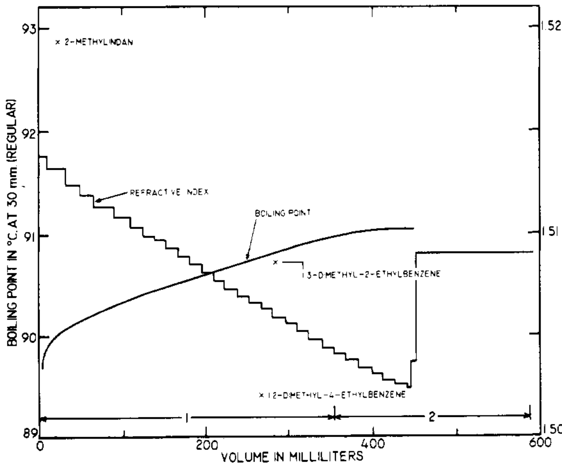


Figure 12. Portion 7 (Figure 4)

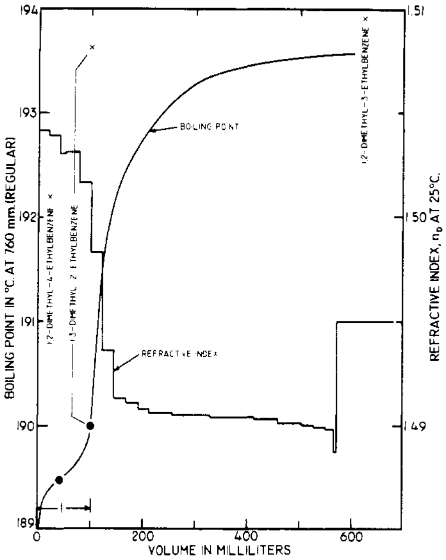


Figure 13. Portion 8 (Figure 5)

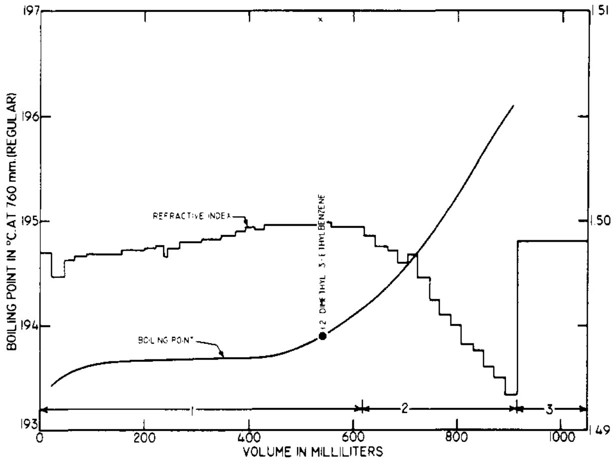


Figure 14. Portion 9 (Figures 5 and 6)

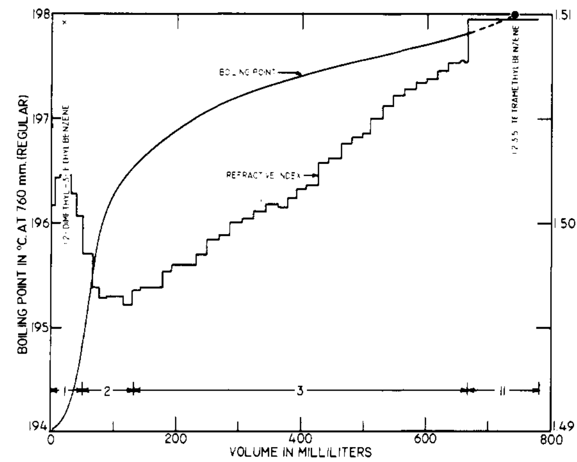


Figure 15. Portion 10A (Figures 5 and 6 and text)

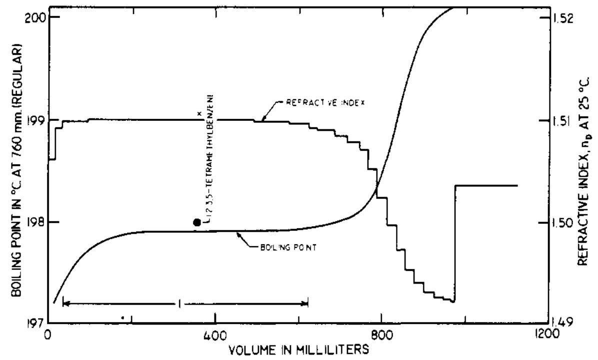


Figure 16. Portion 11 (Figures 6, 7, and 15)

Distillation of Concentrates

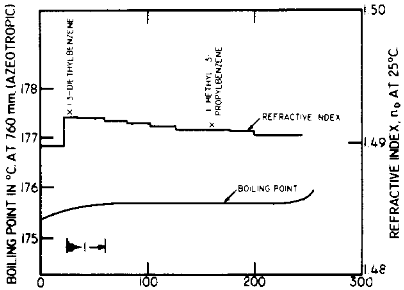


Figure 17. 1,3-Diethylbenzene(azeotropic)

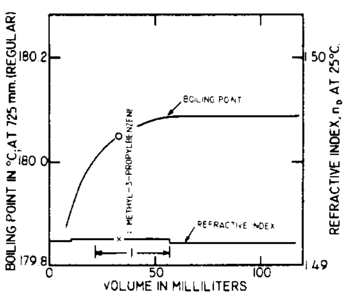
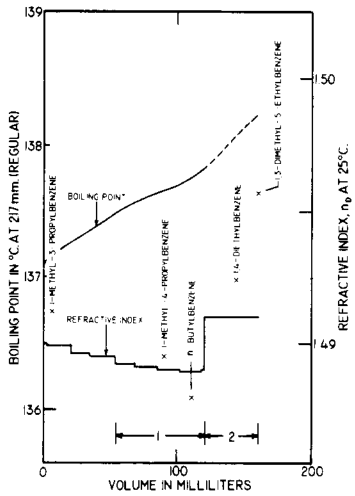


Figure 18. 1-Methyl-3-propylbenzene

Figure 19. 1-Methyl-4-propylbenzene and n-butylbenzene



The amount of the individual hydrocarbons were computed from the results of spectrographic analyses made on selected fractions by the Research Laboratory of the Humble Oil and Refining Co., together with information on the volume, boiling point, and refractive index of the distillate fractions. In the case of 1,2,4,5-tetramethylbenzene, the content was determined, in part, from the amount separated by crystallization. Results of the spectrographic analyses of portions 3, 4, 6 to 9, and 11 are given in Table I.

In some instances the foregoing operations gave satisfactory concentrates of the individual components. In other cases, additional processing was required to obtain the "best" samples of the individual compounds.

Table I. Results of Spectrographic Analyses of Seven Portions[a]

Compound	3	4	6	7	8	9	11
	Percentage by Volume in Portion						
n-Butylbenzene	3.2						
Propylbenzenes							
1-Methyl-4-	2.4						
1-Methyl-2-	66.8	20.0	0.9				
Ethylbenzenes							
1,2-Di-	0.0						
1,4-Di-	1.4	1.1					
1,3-Dimethyl-5-	12.3	2.3					
1,4-Dimethyl-2-	9.5	54.0	4.9	2.6			
1,3-Dimethyl-4-	1.6	18.7	30.2	7.4			
1,2-Dimethyl-4-		0.2	37.5	37.6			
1,3-Dimethyl-2-			2.2	10.5			
1,2-Dimethyl-3-			1.7	3.1			
Tetramethylbenzenes							
1,2,4,5-			(2.0)	(4.1)			
1,2,3,5-			(1.3)	(2.1)			
1-Methylindan	(1.5)	0.7	4.8	12.8			
2-Methylindan	0.0	0.6	6.3	7.1			
C_{10} Alkylbenzenes					23.5	33.5	78.8
C_{11} Alkylbenzenes					71.6	59.6	19.4
C_{10} Alkylindans					1.9		(0.2)
C_{11} Alkylindans					2.8	7.1	1.3

[a] Values for portions 3, 4, 6, and 7 were by infrared spectrometer. For portions 8, 9, and 11, the total C_{10} alkylbenzenes, C_{10} alkylindans, C_{11} alkylbenzenes, and C_{11} alkylindans were by mass spectrometer.

ISOLATION OF INDIVIDUAL HYDROCARBONS

1,3-Diethylbenzene and 1-Methyl-3-propylbenzene originated principally in portion 1 (Figure 2). All of portion 1, in charges of 200 ml., was fractionated by adsorption with silica gel in a column 52 feet in length and 3/4 inch in inside diameter (*3*). These fractions were blended in two lots: lot 1a comprising material which crystallized at temperatures near −95° C., and lot 1b which could not be crystallized. Results of the spectrographic analyses of these lots by infrared are given in Table II. Both lots were distilled regularly. The lowest boiling part of the distillate from lot 1b was combined with 150 ml. of material from the tail end of a distillation of the 170° to 180° C. aromatic portion (*2*) and the blend distilled azeotropically. Results are given in Figure 17. Portion 1 (Figure 17) was selected as the best concentrate of 1,3-diethylbenzene. The composition of this portion, in volume per cent, from spectrographic analysis by infrared, was: 1,3-diethylbenzene, 60.5; 1-methyl-3-propylbenzene, 37.2; and n-butylbenzene, 2.2.

Results of the distillation of lot 1a are given in Figure 18. Portion 1 (Figure 18) was selected as the best sample of 1-methyl-3-propylbenzene. Its purity was found from measurements of freezing point to be 92 mole %.

n-Butylbenzene and 1-Methyl-4-propylbenzene originated principally in portion 2 (Figure 2). All of portion 2, in charges of 200 ml. was fractionated by adsorption with silica gel in a 52-foot column (*3*). The fractions from this operation were blended according to refractive index, n_D^{25}, as follows: lot 2a, from 1.4885 to 1.4904; lot 2b, from 1.4905 to 1.4923; lot 2c, from 1.4924 to 1.4930; and lot 2d, from 1.4931 to 1.4990. The results of the spectrographic analyses of these lots by infrared are given in Table II. Lot 2a, containing the highest concentration of n-butylbenzene and 1-methyl-4-propylbenzene, was distilled at 217 mm. of

Table II. Results of Infrared Spectrographic Analyses of Selected Fractions

	Lot Number						Portion Number			
							1	2	1	2
	1a	1b	2a	2b	2c	2d	Figure 20		Figure 21	
Compound	Percentage by Volume in Portion									
1,3-Diethylbenzene	29.1	33.6	6.6	9.8	4.2	3.5	2.2	15.9		
1-Methyl-3-propylbenzene	68.8	58.1	15.3	23.9	10.5	7.7	1.2	41.7	0.2	1.1
n-Butylbenzene	1.0	1.3	31.5	17.8	13.6	7.9	51.0	17.0	9.3	1.1
1-Methyl-4-propylbenzene	0.0	0.9	29.5	14.5	13.9	7.8	41.3	19.2	3.2	2.8
1,2-Diethylbenzene	0.0	0.0	(0.1)	(0.1)	0.4	24.7	0.0	0.0	0.0	63.5
1,3-Dimethyl-5-ethylbenzene	0.0	0.7	10.7	29.7	53.6	42.6	0.4	3.4	87.3	29.0
1,4-Diethylbenzene			5.4	3.7	3.8	3.6	3.9	2.8	0.0	2.5

mercury (Figure 19). Portion 1 (Figure 19), believed to be the richest part of the distillate in the two compounds, was fractionated by adsorption with silica gel in a column 63.3 feet in length and 3/4 inch in inside diameter (Figure 20). Results of the spectrographic analyses by infrared of the first and last fraction (portions 1 and 2, respectively, of Figure 20) are given in Table II. Portion 1, with 51% *n*-butylbenzene and 41.3% 1-methyl-4-propylbenzene, was selected as the best concentrate of the two compounds.

1,2-Diethylbenzene and 1,3-Dimethyl-5-ethylbenzene could not be concentrated by distillation at 30 mm. of mercury of lot 2c and lot 2d, respectively. The best samples of these compounds were obtained by fractionation by adsorption with silica gel in a 63.3-foot column, of a 100-ml. charge consisting of a blend of selected portions of the distillate from these two lots. Results of the processing by adsorption are given in Figure 21. Spectrographic analyses by infrared of portions 1 and 2 (Figure 21) are given in Table II. Portion 1 contained 87% of 1,3-dimethyl-5-ethylbenzene and portion 2 contained 63.5% of 1,2-diethylbenzene.

1,4-Diethylbenzene was present in low concentrations in lots 2a, 2b, 2c, and 2d (Table II), with lot 2a containing the highest concentration, 5.4%. The residue from the distillation of lot 2a (portion 2 in Figure 19) was found by spectrographic analysis by infrared to be constituted as follows in volume per cent: 1-methyl-4-propylbenzene, 35.4; *n*-butylbenzene, 20.0; 1,3-dimethyl-5-ethylbenzene, 34.1; and 1,4-diethylbenzene, 9.3. This was the highest concentration obtained for 1,4-diethylbenzene.

1-Methyl-2-propylbenzene originated in portion 3 Figures 2 to 4). Azeotropic distillation of this portion gave the results shown in Figure 8. From measurements of freezing points, portion 1 (Figure 8) was found to contain 84 mole % of 1-methyl-2-propylbenzene.

1,4-Dimethyl-2-ethylbenzene orignated in portion 4 (Figure 4). Regular distillation of this portion at a pressure of 217 mm. of mercury gave the results shown in Figure 9. From measurements of freezing points, portion 1 (Figure 9) was found to contain 75 mole % of 1,4-dimethyl-2-ethylbenzene.

1,3-Dimethyl-4-ethylbenzene originated principally in portions 5 and 6 (Figure 4). Results of the regular distillation of portions 5 and 6 at a pressure of 217 mm. of mercury are shown in Figures 10 and 11, respectively. From measurements of freezing points, portion 1 (Figure 10) was found to contain 61 mole % of 1,3-dimethyl-4-ethylbenzene. A second sample resulted from the azeotropic distillation of a blend of portion 2 (Figure 10) and portion 1 (Figure 11) as shown in Figure 22. Portion 1 (Figure 22) comprised the second sample of this compound.

1,2-Dimethyl-4-ethylbenzene originated principally in portions 6 to 8 (Figures 4 and 5). It is closely associated with 1,3-dimethyl-4-ethylbenzene, 1,3-dimethyl-2-ethylbenzene, 1-methylindan, and 2-methylindan. Results of the distillation of portion 7, at 30 mm. of mercury, are given in Figure 12, and those of portion 8, at 760 mm. of mercury are given in Figure 13.

Portions 1 and 2 (Figure 12) were distilled azeotropically. The results are given in Figures 23 and 24, respectively. Several concentrates of 1,2-dimethyl-4-ethylbenzene were obtained. From measurements of freezing points, portion 1 (Figure 24) was found to contain 89 mole % of 1,2-dimethyl-4-ethylbenzene. A second concentrate was obtained from the regular distillation of a blend of portion 1 (Figure 13), portion 1 (Figure 22) and portion 1 (Figure 23). The results of this distillation are shown in Figure 25. Portion 1 (Figure 25) comprised this second concentrate. A third concentrate resulted from the azeotropic distillation of portion 2 (Figure 25) as shown in Figure 26.

1,3-Dimethyl-2-ethylbenzene originated principally in portions 7 and 8. It was concentrated as a result of the distillations described in the preceding section. Portion 2 (Figure 24) was selected as the best sample, and from measurements of freezing points was found to contain 60 mole % of 1,3-dimethyl-2-ethylbenzene.

1-Methylindan and 2-Methylindan were found in material boiling about 1° C. below their normal boiling points. They originated in portions 6 and 7 (Figures 4 and 5). The azeotropic distillations already described concentrated these compounds near the tail end of the distillate (Figures 22 to 24 and 26). Portion 4 (Figure 22) and portion 4 (Figure 23) were examined spectrographically without additional fractionation. Portion 3 (Figure 22) and portions 2 and 3 (Figure 23) were fractionated by adsorption with silica gel in a 4-foot column, and selected portions of the filtrate examined spectrographically. Results of the fractionation of portion 2 (Figure 23) by adsorption are given in Figure 27. Portion 1 (Figure 27) comprised the material selected for the spectrographic examination. Results of the spectrographic examinations are given in Tables III and IV. The examination by mass spectrometer showed the presence of both C_{10} indans and indenes in these samples. The 1-and 2-methylindans oxidize readily on exposure to air, with the oxidation product losing water at 180° C. This probably accounts for the presence in these samples of indenes which are not believed to occur in the original petroleum. The maximum content of methylindan (34%) obtained was for the sample derived by adsorption from portion 3 (Figure 22).

1,2-Dimethyl-3-ethylbenzene originated principally in portions 9 and 10 (Figures 5 and 6). Results of the regular distillation of portions 9 and 10A (the part of portion 10 remaining after the removal of 1,2,4,5-tetramethylbenzene by crystallization) are given in Figures 14 and 15, respectively. Azeotropic distillation of portion 1 (Figure 14) gave the results shown in Figure 28. From measurements of freezing points, portion 3 (Figure 28) was found to contain 84 mole % of 1,2-dimethyl-3-ethylbenzene. A second sample was obtained by azeotropic distillation of a blend of portion 1 (Figure 15) and portion 2 (Figure 28). Results are given in Figure 29. Portion 2 from this figure comprised the second sample.

1,2,4,5-Tetramethylbenzene was found in portion 10

Fractionations by Adsorption

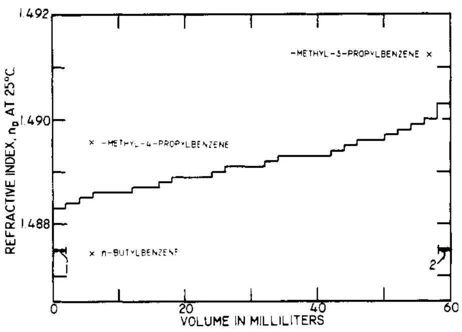
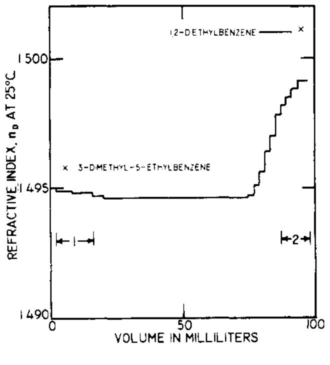


Figure 20. Portion 1 (Figure 19)

Figure 21. A concentrate of 1,3-dimethyl-5-ethylbenzene and 1,2-diethylbenzene



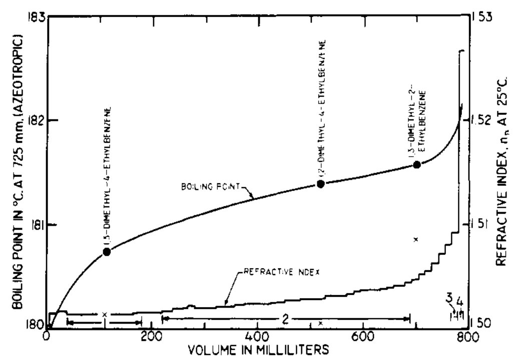
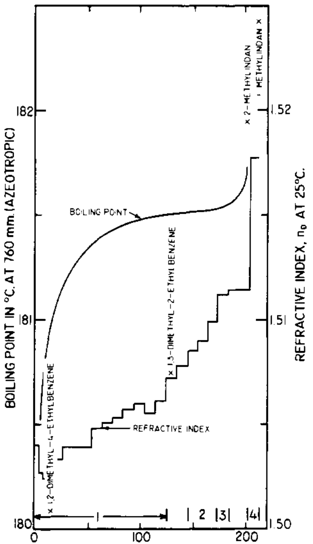


Figure 22. Portion of Figure 10 plus Portion 1 of Figure 11

Figure 23. Portion 1 of Figure 12



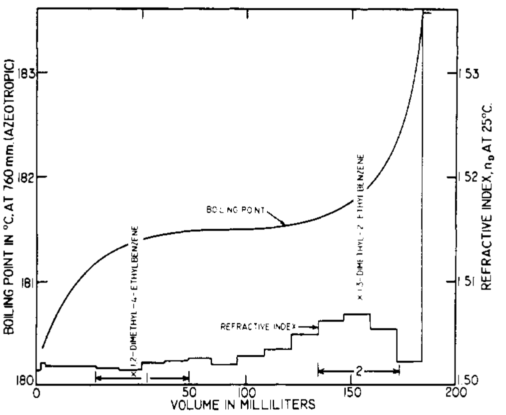


Figure 24. Portion 2 of Figure 12

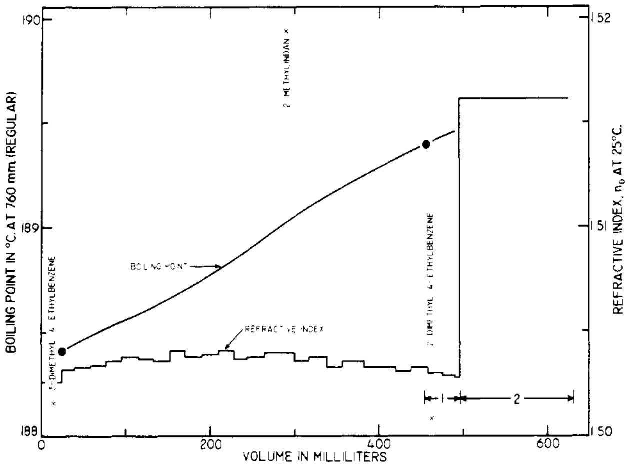
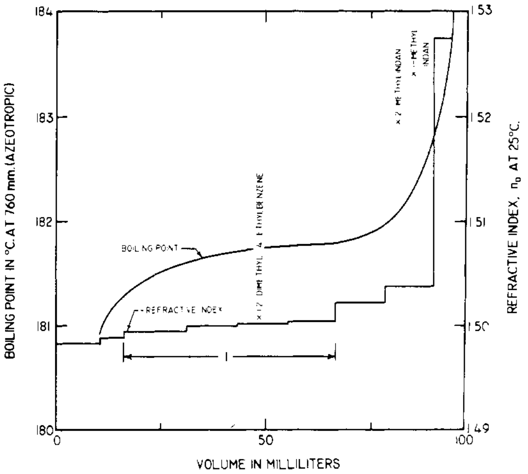


Figure 25. Regular distillation of a blend of Portion 1 of Figure 13, Portion 1 of Figure 22, and Portion 1 of Figure 23

Figure 26. Azeotropic distillation of Portion of Figure 25



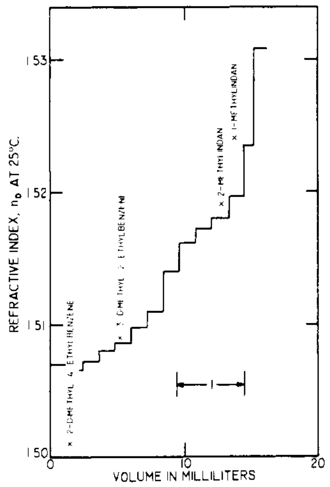


Figure 27. Fractionation by adsorption of a methylindan concentrate (Portion 2 of Figure 23)

Table III. Results of Mass Spectrographic Analyses of Concentrates of Methylindans[a]

	Portion Number				
	3[b]	4	2[b]	3[b]	4
	Figure 22		Figure 23		
Compounds	Percentage by Volume				
C_{10} alkylbenzenes	64	41	72	60	45
C_{10} alkylindans	34	26	22	21	25
C_{10} alkylindenes	2	30	4	3	14

[a] These samples contained small amounts of C_{11} hydrocarbons.
[b] By adsorption.

Table IV. Results of Infrared Spectrographic Analyses of Concentrates of Methylindans

Compound	Portion 3, Figure 22, by Adsorption	Portion 2, Figure 23, by Adsorption
	Percentage by Volume	
1-Methylindan	23	12
2-Methylindan	10	15
1,2-Dimethyl-4-ethylbenzene	31	45
1,3-Dimethyl-2-ethylbenzene	32	25

(Figures 5 and 6), which contained crystals at room temperature. Repeated crystallization of this material, with the aid of centrifuging, both with and without acetone, as a solvent, separated a sample containing 97.2 mole % of 1,2,4,5-tetramethylbenzene. A total of 405 ml., containing 90 mole % or more, was obtained. The mother liquors remaining after crystallization at −20° C., designated portion 10A, were distilled regularly. Results are given in Figure 15. Azeotropic distillation of a blend of portion 3 (Figure 14) and portion 3 (Figure 15) gave the results shown in Figure 30. The composition of the charge for this distillation in volume per cent, from mass spectrographic analysis, was found to be as follows: C_{10} alkylbenzenes, 67.2; C_{11} alkylbenzenes, 32.1; C_{10} alkylindans, (0.2); and C_{11} alkylindans, 0.5. An additional 60 ml. of 1,2,4,5-tetramethylbenzene was obtained by crystallization of the portion indicated in Figure 30.

Azeotropic Distillation

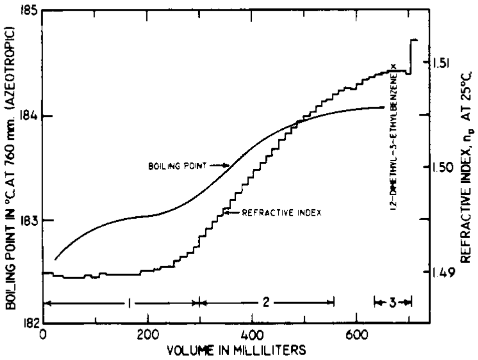


Figure 28. Portion of Figure 14

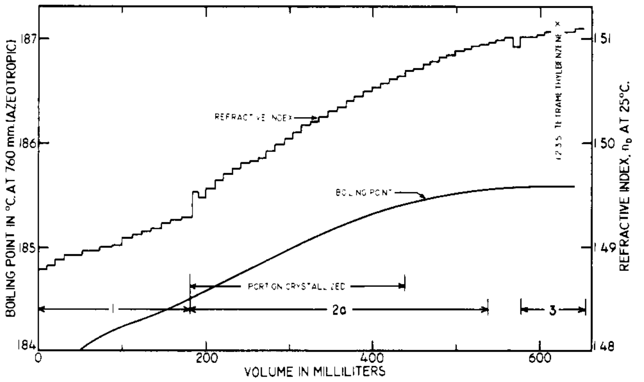


Figure 30. Portion 3 of Figure 14 plus Portion 3 of Figure 15

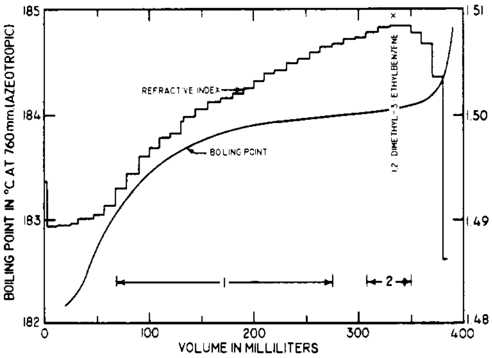


Figure 29. Portion 1 of Figure 15 plus Portion 2 of Figure 28

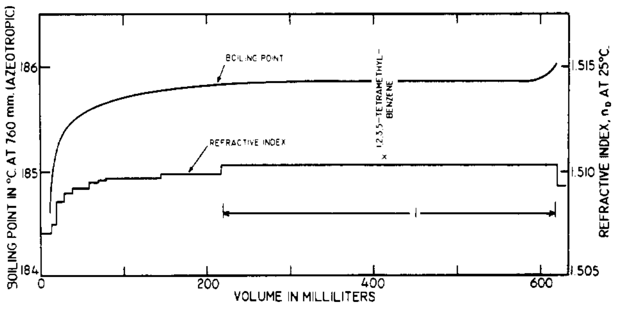


Figure 31. Portion 1 of Figure 16

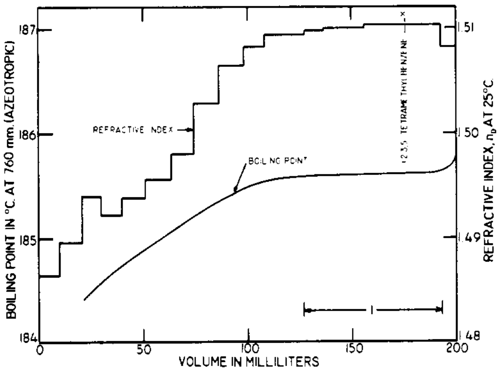


Figure 32. Portion 2a of Figure 30

Table V. Summary of 17 Hydrocarbons Found in the 180° to 200° C. Aromatic Fraction of Petroleum

Compound	Boiling Point of Pure Compound at 1 Atm., ° C.	Highest Concentration Isolated,[a] Mole %	Estimated Amount in Original Petroleum, Vol. %
1,3-Diethylbenzene	181.10	61[b]	0.033
1-Methyl-3-propylbenzene	181.80	92	0.066
n-Butylbenzene	183.27	51[b]	0.026
1-Methyl-4-propylbenzene	183.30	43[b]	0.027
1,2-Diethylbenzene	183.42	64[b]	0.005
1,3-Dimethyl-5-ethylbenzene	183.58	87[b]	0.063
1,4-Diethylbenzene	183.78	9[b]	0.007
1-Methyl-2-propylbenzene	184.80	84	0.046
1,4-Dimethyl-2-ethylbenzene	186.83	75	0.041
1,3-Dimethyl-4-ethylbenzene	188.20	61	0.050
1,2-Dimethyl-4-ethylbenzene	189.48	89	0.057
1,3-Dimethyl-2-ethylbenzene	190.01	60	0.014
1-Methylindan	190.6	34[b]	0.022
2-Methylindan	191.4		
1,2-Dimethyl-3-ethylbenzene	193.91	84	0.036
1,2,4,5-Tetramethylbenzene	196.80	97	0.052
1,2,3,5-Tetramethylbenzene	198.00	96	0.12
C_{11} alkylbenzenes	. . .	. . .	0.15
C_{11} alkylindans	. . .	. . .	0.015
Total			0.83

[a] Determined from freezing points except those marked [b].
[b] From spectrographic analyses.

1,2,3,5-Tetramethylbenzene originated principally in portion 11 (Figures 6, 7, and 15). Results of the regular distillation of portion 11 are given in Figure 16. Azeotropic distillation of portion 1 (Figure 16) gave the results shown in Figure 31. From measurements of freezing points, portion 1 (Figure 31) was found to contain 95.4 mole % of 1,2,3,5-tetramethylbenzene. Two additional samples of this compound were obtained. One of these comprising portion 3 (Figure 30) resulted from processing already described. The other resulted from the azeotropic distillation of portion 2a (Figure 30). Results are given in Figure 32. Portion 1 comprised this third sample.

RESULTS

Table V summarizes the information regarding the 17 hydrocarbons found in the 180° to 200° C. fraction of this petroleum. The alkylbenzenes present in largest amount are the tetramethylbenzenes, followed in decreasing order by the dimethylethylbenzenes, the methyl-*n*-propylbenzenes, the diethylbenzenes, and the butylbenzenes. That is, for a given number of substituent carbon atoms, the more abundant alkylbenzenes are those with more and smaller alkyl groups.

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