

# Separation of 2,3-Dimethylpentane, 1,*cis*-3-Dimethylcyclopentane, and 3-Ethylpentane from Petroleum<sup>1</sup>

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This report describes the separation of 3-ethylpentane and the fractionation of 2,3-dimethylpentane and 1,*cis*-3-dimethylcyclopentane from the aromatic-free fraction of petroleum normally boiling in the range 89° to 94° C. These three compounds, together with the four hydrocarbon compounds previously separated, constitute substantially all of the material of this fraction of petroleum. For these seven compounds, the normal boiling points (of high-purity samples not from the present investigation) and the estimated amounts by volume in the original Ponca, Oklahoma, crude petroleum are as follows: 2,3-dimethylpentane, 89.78° C, 0.1 percent; 2-methylhexane, 90.05° C, 0.7 percent; 1,*trans*-3-dimethylcyclopentane, 90.77° C, 0.9 percent; 1,*cis*-3-dimethylcyclopentane, 91.72° C, 0.2 percent; 3-methylhexane, 91.85° C, 0.5 percent; 1,*trans*-2-dimethylcyclopentane, 91.87° C, 0.5 percent; and 3-ethylpentane, 93.47° C, 0.05 percent.

## I. Introduction

As part of the work of the API Research Project 6 at the National Bureau of Standards on the fractionation and analysis of hydrocarbons in petroleum [1, 2],<sup>2</sup> the program has been completed on that part of petroleum normally boiling between 89° and 94° C. In earlier work [3, 4], 2-methylhexane, 1,*trans*-3-dimethylcyclopentane, 1,*trans*-2-dimethylcyclopentane, and 3-methylhexane were separated from this fraction, and in the present investigation 2,3-dimethylpentane, 1,*cis*-3-dimethylcyclopentane, and 3-ethylpentane have been determined.<sup>3</sup> This report describes the fractionation of the latter three hydrocarbons and gives the estimated amounts of all seven hydrocarbon components that comprise the aromatic-free fraction of petroleum normally boiling in the range 89° to 94° C.

## II. Material Analyzed

The API Research Project 6 at the National Bureau of Standards has had under investigation

<sup>1</sup> 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."

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>3</sup> See reference [5] for the naming of geometric isomers of the polyalkyl cycloparaffins.

since 1928 a large quantity of a representative petroleum taken from a well at Ponca, Okla. [1, 2, 6]. All of the material from the original petroleum normally boiling between 89° and 94° C remaining after the previous treatment [3, 4, 7] was blended together for analysis, with the exception of small lots of approximately 50 ml each of the best samples of 2-methylhexane, 1,*trans*-3-dimethylcyclopentane, 1,*trans*-2-dimethylcyclopentane, and 3-methylhexane separated in the previous processing [3, 4]. Before the beginning of the present investigation, the material was again filtered through silica gel [8] to remove traces of toluene and produce a mixture containing only paraffins and cycloparaffins.

## III. Method of Analysis and Results

This blend of material normally boiling between 89° and 94° C was distilled analytically at high efficiency. Following the initial distillation shown in figure 1, parts *A*, *B*, *C*, and *D* of the distillate were further processed to fractionate 2,3-dimethylpentane, 1,*cis*-3-dimethylcyclopentane, and 3-ethylpentane, as listed in table 1. Reference [9] gives a description of the distilling columns used.

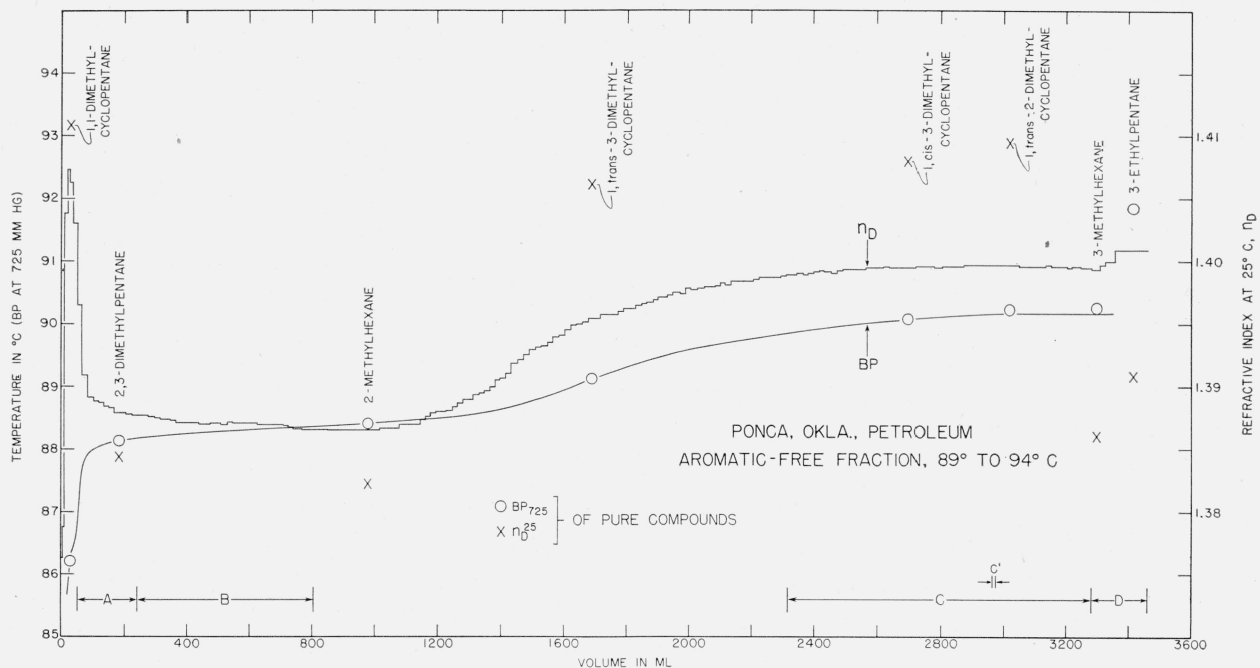


FIGURE 1. Distillation of the 89° to 94° C (aromatic-free) fraction of petroleum.

The ordinate scale on the right gives the refractive indices of the fractions of distillate, and the ordinate scale on the left gives the boiling point of the distillate at 725 mm Hg. The scale of abscissas gives the volume of distillate in milliliters. The portions *A* to *D*, enclosed with arrows, were redistilled. The distillate fraction, *C'*, was analyzed by spectrographic infrared absorption measurements, the results of which are given in table 2.

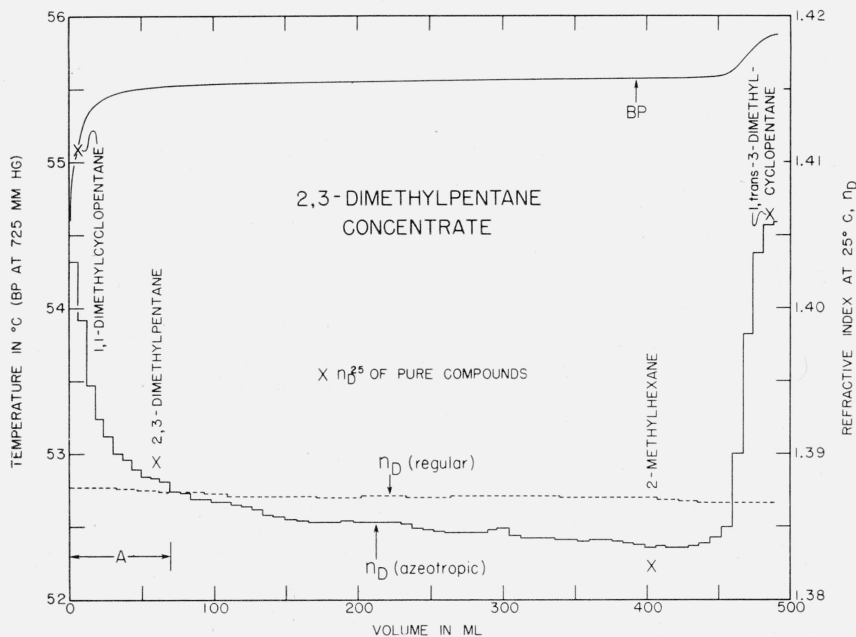


FIGURE 2. Distillation of the 2,3-dimethylpentane concentrate (part *B*, fig. 1).

The ordinate scale on the right gives the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate, and the ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm Hg. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The portion *A*, enclosed with arrows, was redistilled. The broken curve refers to the previous distribution of the refractive index of this material in the regular distillation (shown by part *B* of fig. 1).

TABLE 1. Information on the distillation for the analysis and separation of 2,3-dimethylpentane, 1,cis-3-dimethylcyclopentane, and 3-ethylpentane from the aromatic-free fraction of petroleum normally boiling in the range 89° to 94° C.

Material	Distillation									
	Dis- tilling <sup>a</sup> column number	Number of equiva- lent theoretical plates at total reflux (approx- imately)	Reflux ratio (approx- imately)	Rate of col- lection of dis- tillate	Pressure of dis- tillation (con- trolled)	Kind of distillation	Azeotrope-forming substance, if used, and its volume	Vol- ume of hy- dro- carbon charged	Volume of each fraction of dis- tillate	Re- sults plotted in figure
				ml/hr	mm Hg			ml	ml	
84° to 94° C (aromatic-free) fraction of petroleum.	<sup>b</sup> 3A	200	190/1	4.2	725	Regular		3,530	17	1
2,3-Dimethylpentane concentrate (part B, fig. 1).	1A	150	270/1	1.1	725	Azeotropic	Methanol, 700 ml	550	12	2
2,3-Dimethylpentane concentrate (part A, figs. 1 and 2).	1A	150	270/1	1.1	725	Regular		235	12	3
1,cis-3-Dimethylcyclopentane concen- trate (part C, fig. 1).	1A	150	200/1	1.5	725	Azeotropic	Methanol, 750 ml	878	11	4
1,cis-3-Dimethylcyclopentane concen- trate (part A, fig. 4).	1A	150	150/1	0.5	54	Regular		202	13	5
3-Ethylpentane concentrate (part D, fig. 1).	1A	150	300/1	1.0	725	do		198	7	6
3-Ethylpentane concentrate (part A, fig. 6).	1A	150	300/1	1.0	725	Azeotropic	Methanol, 150 ml	40	6	7

<sup>a</sup> For further details, see reference [9].

<sup>b</sup> Same as column 4 in reference [9].

2,3-Dimethylpentane was fractionated by azeotropic distillation with methanol followed by regular distillation, the results of which are shown in figures 2 and 3. In the azeotropic distillation, the methanol, which comprised about 40 percent by volume of the distillate, was extracted from the hydrocarbon portion by three cold water extractions in a separatory funnel. The best lot from the distillate shown in figure 3 was selected on the

basis of boiling point and refractive index as having the highest concentration of 2,3-dimethylpentane. This fraction was examined by spectrographic infrared absorption measurements by the Humble Oil and Refining Company, Houston, Texas, and found to contain 57 percent by volume of 2,3-dimethylpentane. The results are given in table 2.

TABLE 2. Results of the spectrographic infrared absorption measurements<sup>a, b</sup> of selected samples from the aromatic-free fraction of Ponca, Oklahoma, petroleum normally boiling in the range 89° to 94° C

Identification of sample	3, 3-Dimethylpentane	1, 1-Dimethylcyclopentane	2, 3-Dimethylpentane	2-Methylhexane	1, trans-3-Dimethylcyclopentane	1, cis-3-Dimethylcyclopentane	3-Methylhexane	1, trans-2-Dimethylcyclopentane	3-Ethylpentane	n-Heptane	Methylcyclohexane
	Percentage by volume in the sample										
Part C'; figure 1 <sup>b</sup>				2	7	15	37				
2,3-Dimethylpentane; figure 3 <sup>a</sup>		1	57	37	3	2	0	0			
Part A'; figure 4 <sup>a</sup>				0	3	21	54	22			
Part B; figure 4 <sup>a</sup>				0	3	23	42	32			
Part C; figure 4 <sup>a</sup>				0	2	21	19	58			
Part D; figure 4 <sup>a</sup>				0	2	6	0	92			
Part A; figure 5 <sup>a</sup>				4	19	43	9	25			
Part B; figure 5 <sup>a</sup>				2	8	51	10	29			
Part C; figure 5 <sup>a</sup>				0	7	31	30	32			
3-Ethylpentane; figure 7 <sup>a</sup>						0	0.4	0.8	98.7	0	0

<sup>a</sup> Made by the Humble Oil & Refining Co., Baytown, Tex. A description of the apparatus is given in reference [10].

<sup>b</sup> Made by the Socony-Vacuum Laboratories, Paulsboro, N. J. A description of the apparatus is given in reference [11].

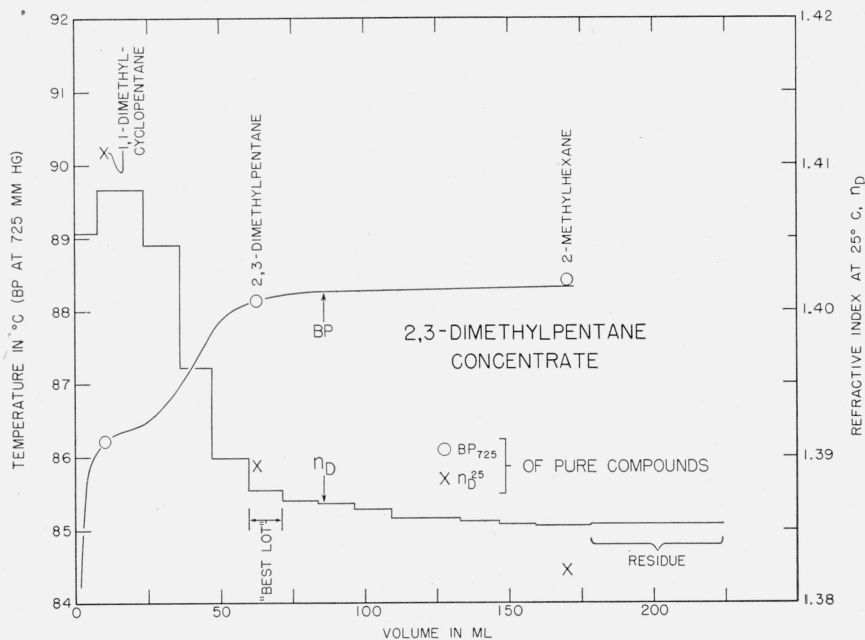


FIGURE 3. Distillation of the 2,3-dimethylpentane concentrate (part A, figs. 1 and 2).

The ordinate scale on the right gives the refractive indices of the fractions of distillate, and the ordinate scale on the left gives the boiling point of the distillate at 725 mm Hg. The scale of abscissas gives the volume of distillate in milliliters. The portion labeled "best lot" was analyzed by spectrographic infrared absorption measurements, the results of which are given in table 2.

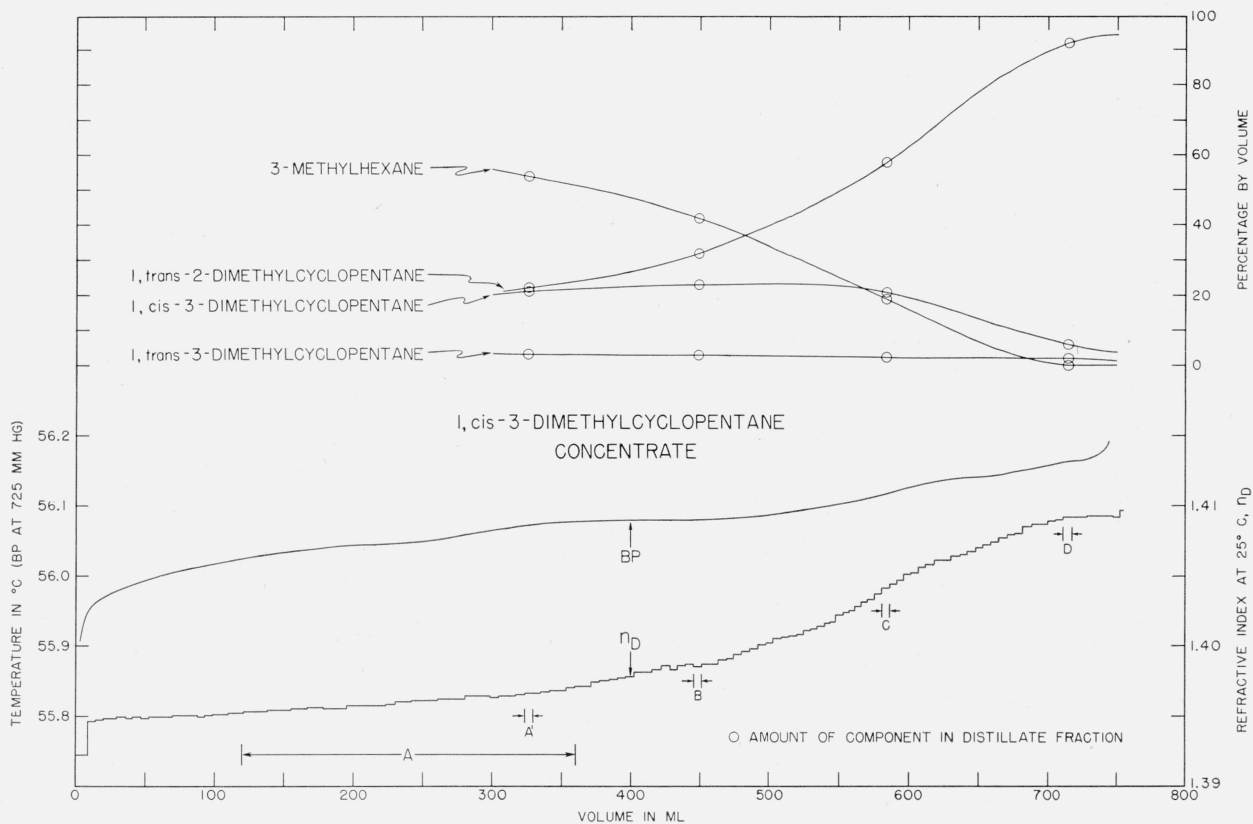


FIGURE 4. Distillation of the 1,cis-3-dimethylcyclopentane concentrate (part C, fig. 1).

The ordinates on the right give, on the lower scale, the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate and, on the upper scale, the percentage by volume of the components in the hydrocarbon portion of the distillate, as determined by spectrographic infrared absorption measurements on fractions labeled A', B, C, and D in the figure. These results are given numerically in table 2 and graphically in the upper portion of the figure. The ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm Hg. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The portion A, enclosed with arrows, was redistilled.

The following conclusions may be drawn from the results of the processing of the 2,3-dimethylpentane concentrates: (a) The regular distillation shown in figure 1 substantially separated the components normally boiling near 92° C from 2,3-dimethylpentane and 2-methylhexane normally boiling near 90° C; (b) azeotropic distillation with methanol was effective in further separating 1,1-dimethylcyclopentane and 1,*trans*-3-dimethylcyclopentane from 2,3-dimethylpentane and 2-methylhexane, as shown in figure 2; (c) the regular distillation following the azeotropic distillation further improved the 2,3-dimethylpentane concentrate with additional removal of lower-boiling 1,1-dimethylcyclopentane, as shown in figure 3; (d) regular and azeotropic distillation at 725 mm Hg effects only a partial separation of the two paraffins, 2,3-dimethylpentane and 2-methylhexane. However, regular distillation at reduced pressure should produce a more effective separation because of the increased difference (approximately 1 deg C) in the boiling points [12] of the two isomers at lower pressures (30 to 50 mm Hg).

Following the regular distillation shown in figure 1, 1,*cis*-3-dimethylcyclopentane was fractionated from the components normally boiling near 92° C by azeotropic distillation with methanol followed by regular distillation at a reduced pressure of 54 mm Hg. The results are shown in figures 4 and 5. Part *B* of the distillate shown in figure 5 contained the highest concentration of 1,*cis*-3-dimethylcyclopentane. This portion was examined by spectrographic infrared absorption measurements by the Humble Oil and Refining Company, Houston, Texas, and found to contain 51 percent by volume of 1,*cis*-3-dimethylcyclopentane. The results are given in table 2.

The following conclusions may be drawn from the processing of the material normally boiling near 92° C with respect to the separation of 1,*cis*-3-dimethylcyclopentane: (a) Azeotropic distillation with methanol, as shown in figure 4 and table 2, produces an appreciable separation in the two dimethylcyclopentanes, one from the other, resulting in a nine-fold change in the composition of the two isomers in the distillate, as well as effectively removing 3-methylhexane from 1,*trans*-2-dimethylcyclopentane; (b) the regular distillation at a pressure of 54 mm Hg, as shown in figure 5, effectively removes the 3-methylhexane from the

cycloparaffins because of the greater difference in the boiling points [4, 12] at the reduced pressure between the paraffin, 3-methylhexane, and the cycloparaffins, 1,*cis*-3-dimethylcyclopentane and 1,*trans*-2-dimethylcyclopentane.

3-Ethylpentane was separated from the undistilled portion, *D*, in figure 1, by regular distillation followed by azeotropic distillation with methanol. The results are shown in figures 6 and 7, respectively. The best lot from the distillate shown in figure 7 was selected on the basis of boiling point and refractive index as having the highest concentration of 3-ethylpentane. This lot was examined by spectrographic infrared absorption measurements by the Humble Oil and Refining Co., Baytown, Tex., and found to contain 98.7 percent by volume of 3-ethylpentane. The results are given in table 2.

The following conclusion may be drawn from the processing of the 3-ethylpentane concentrates: (a) This compound, which occurs in small amount in petroleum, is easily separated by regular and azeotropic distillation.

#### IV. Amounts in the Crude Petroleum

The calculation of the amounts by volume of the seven compounds in the aromatic-free fraction of Ponca, Okla., petroleum, normally boiling between 89° and 94° C, was made using the data from the analysis of seven representative crude petroleums [13, 14, 15] supplemented by the results of the present investigation, including the spectrographic infrared absorption measurements on selected fractions as listed in table 2.

The spectrographic data served to establish the relative amounts of 1,*cis*-3-dimethylcyclopentane and 1,*trans*-2-dimethylcyclopentane, and of 2,3-dimethylpentane and 2-methylhexane. The data on boiling point and refractive index as a function of volume of distillate were utilized to the fullest extent of their precision by plotting the data on expanded scales of temperature, refractive index, and volume for use in the calculation of the amounts of the individual components as described in reference [16].

The ratios of 2,3-dimethylpentane to 2-methylhexane and of 1,*cis*-3-dimethylcyclopentane to 1,*trans*-2-dimethylcyclopentane found in the present investigation are considered to be representative of the original petroleum on the assumption

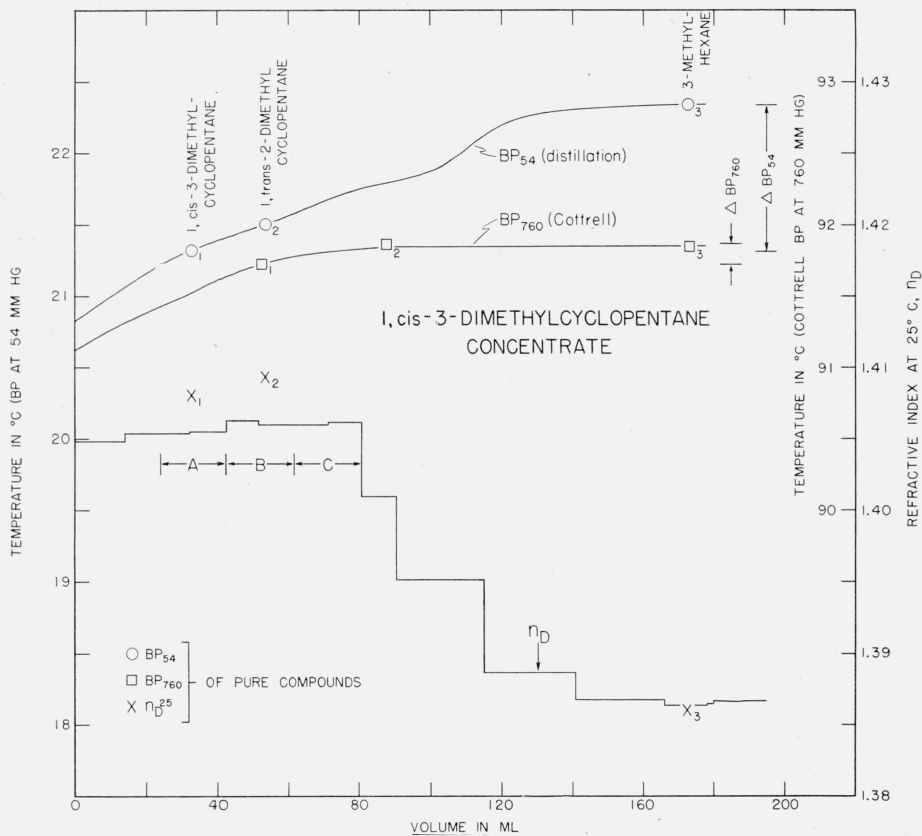


FIGURE 5. Distillation of the 1,cis-3-dimethylcyclopentane concentrate (part A, fig. 4).

The ordinates on the right give, on the outer scale, the refractive indices and, on the inner scale, the Cottrell boiling points at 760 mm Hg of the fractions of the distillate. The ordinate scale on the left gives the boiling point of the distillate at 54 mm Hg. The scale of abscissas gives the volume of distillate in milliliters. The portions A, B, and C, enclosed with arrows, were analyzed by spectrographic infrared absorption measurements, the results of which are given in table 2. The numbers accompanying the boiling point and refractive index values shown in the figure refer to the following: (1) to 1,cis-3-dimethylcyclopentane, (2) to 1,trans-2-dimethylcyclopentane, and (3) to 3-methylhexane.

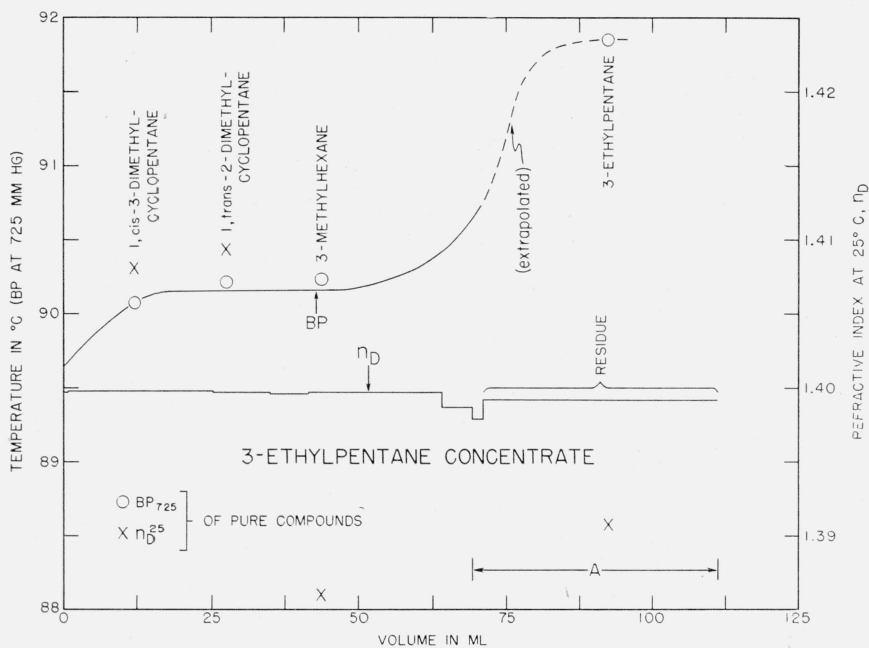


FIGURE 6. Distillation of the 3-ethylpentane concentrate (part D, fig. 1).

The ordinate scale on the right gives the refractive indices of the fractions of distillate, and the ordinate scale on the left gives the boiling point of the distillate at 725 mm Hg. The scale of abscissas gives the volume of distillate in milliliters. The portion A, enclosed with arrows, was redistilled.

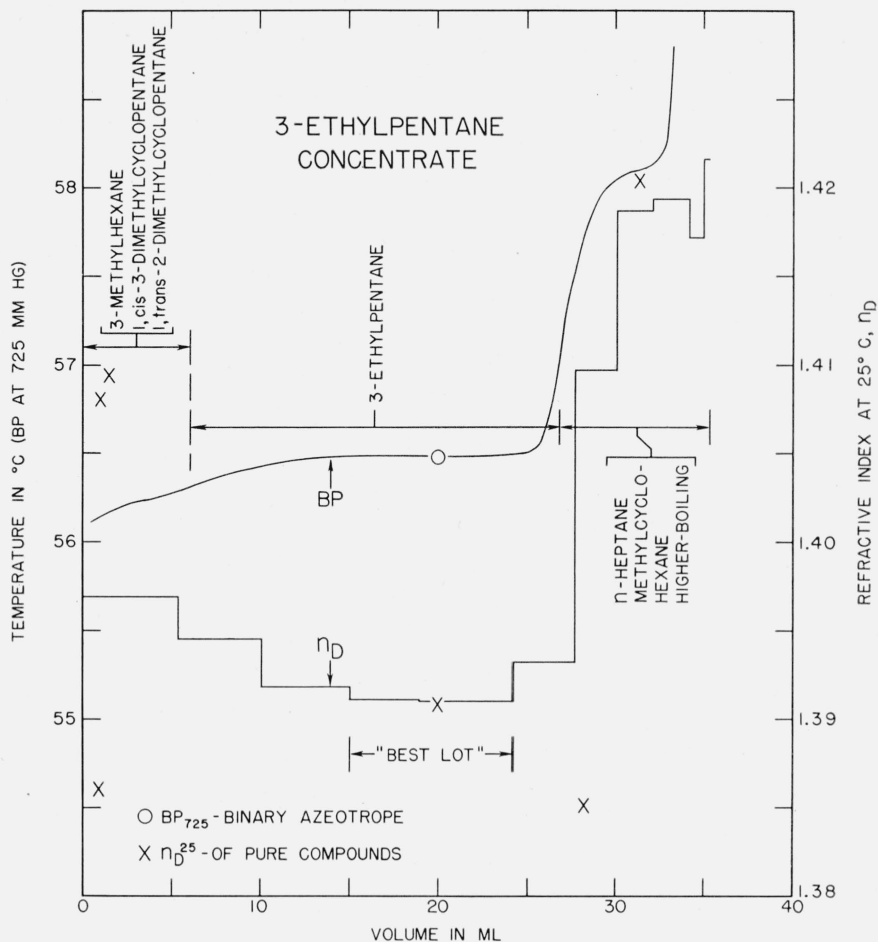


FIGURE 7. Distillation of the 3-ethylpentane concentrate (part A, fig. 6).

The ordinate scale on the right gives the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate, and the ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm Hg. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The portion labeled best lot was analyzed by spectrographic infrared absorption measurements, the results of which are given in table 2.

that no change in composition of these close-boiling pairs of components, which differ in normal boiling point by 0.27° and 0.15° C [12], occurred during previous processing losses.

The amounts by volume of the seven hydrocarbons in the aromatic-free fraction normally boiling in the range 89° to 94° C and in the original petroleum are give in table 3.

TABLE 3. Amounts of the seven hydrocarbons constituting the 89° to 94° C aromatic-free fraction of the petroleum

Component	Boiling point at 1 atm <sup>a</sup>	Relative amount by volume	Amount in the original crude petroleum <sup>b</sup>
	° C		Percentage by volume
2,3-Dimethylpentane.....	89.78	5	0.1
2-Methylhexane.....	90.05	24	.7
1,trans-3-Dimethylcyclopentane.....	90.77	29	.9
1,cis-3-Dimethylcyclopentane.....	91.72	7	.2
3-Methylhexane.....	91.85	17	.5
1,trans-2-Dimethylcyclopentane.....	91.87	16	.5
3-Ethylpentane.....	93.47	2	.05
Total.....		100	2.95

<sup>a</sup> From reference [17].

<sup>b</sup> For each component, the percentage by volume of the gasoline fraction, 40° to 180° C, is about three times the value in this column.

From the data given in table 3, the following points may be made regarding the composition of the material normally boiling between 89° and 94° C, from the Ponca, Okla., petroleum:

(a) The material is composed entirely of branched paraffins and cycloparaffins in approximately equal amounts.

(b) The relative amounts of the methylhexanes, dimethylpentanes, and ethylpentane are approximately 20, 2, and 1, respectively.

(c) The relative amounts of the three dimethylcyclopentanes are 4, 2, and 1, for the 1,trans-3-, 1,trans-2-, and 1,cis-3- isomers, respectively.

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for the spectrographic infrared absorption measurements reported in table 2 of this paper.

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