U. S. Department of Commerce
National Bureau of Standards

Research Paper RP1800
Volume 38, June 1947

Part of the Journal of Research of the National Bureau of Standards

# Hydrocarbons in the 102° to 108° C Fraction of Petroleum[1,2]

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This report describes the analysis of the hydrocarbons in the 102° to 108° C aromatic-free fraction of petroleum, which is shown to be composed substantially of the following three compounds (normally boiling at the temperature indicated): Ethylcyclopentane at 103.5° C; 1,1,3-trimethylcyclopentane at 104.9° C; and 2,2-dimethylhexane at 106.8° C. The amounts of these three compounds in the original Ponca, Okla. crude petroleum are estimated to be, respectively, 0.1%, 0.3%, and 0.01 percent by volume.

## I. Introduction

In continuation of the work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the fractionation and analysis of hydrocarbons in petroleum [1],* work was completed on the resolution of that part of the petroleum normally boiling between 102° and 108° C. On the assumption that the possible components in the original crude petroleum are hydrocarbons of the paraffin, cyclopentane, cyclohexane, and aromatic series, the aromatic-free fraction of petroleum of this boiling range could contain only the following three compounds.[3] Ethylcyclopentane at 103.5° C, 1,1,3-trimethylcyclopentane at 104.9° C, and 2,2-dimethylhexane at 106.8° C. The earlier work in this laboratory [5] on the material of this boiling range was handicapped by lack of the highly efficient means of distillation available for the present investigation [6].

This report describes the analysis of the hydrocarbons in the 102° to 108° C aromatic-free fraction of petroleum, which is shown to be composed substantially of the above-mentioned three compounds.

## II. Material Analyzed

The American Petroleum Institute Research Project 6 at the National Bureau of Standards has had under investigation since 1928 a large quantity of petroleum taken from a well at Ponca, Okla. [1, 7]. The material analyzed in the present investigation constituted that part of this original petroleum normally boiling between 102° and 108° C. From this petroleum there has previously been separated methylcyclohexane (at 100.9° C) [8] and toluene (normally boiling at 110.6° C but actually spread over much lower boiling material) [9]. The status of the material normally boiling in the range 102° to 108° C prior to the present investigation, is described in reference [5]. Before the beginning of the present investigation, the material was made aromatic-free by filtration through silica gel [10].

## III. Method of Analysis and Separation

The material of the original petroleum remaining after the previous treatment [9, 8, 5] was "lined-up" by appropriate preliminary distilla-

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

[3] At the time the first highly efficient analytical distillation of the 102° to 108° C fraction of petroleum was completed in this laboratory in 1942, the existing data in the literature [2, 3] listed 1,1,3-trimethylcyclopentane as normally boiling at 115 to 116° C. It had originally been expected, therefore, that only two compounds, easily separable, would appear in the distillate But a third compound appeared, having a normal boiling point about 1½° C above ethylcyclopentane, with a slightly lower, but still high, refractive index, indicating the new compound to be a cycloparaffin. It was deduced that the latter could only be a $C_8$ alkylcyclopentane, and, further, that the only possible $C_8$ alkylcyclopentane normally boiling near 105° C was 1,1,3-trimethylcyclopentane, the existing literature data to the contrary notwithstanding. These deductions were shortly thereafter confirmed by new data published on the synthesis and properties of 1,1,3-trimethylcyclopentane [4].

* Figures in brackets indicate the literature references at the end of this paper.

tions and blending in order to obtain in one lot of material all the remaining original petroleum normally boiling between 102° and 108° C.

Following the preliminary distillation and blending, five distillations (regular or azeotropic) were performed at high-efficiency and high reflux ratio, as listed in table 1. From appropriate final distillations of this series, small "best lots from petroleum" for ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane were selected for measurement of physical properties and determination of purity.

The purity of the two cycloparaffins, of which there was a sufficient quantity to produce a relatively pure best lot from petroleum, was evaluated from measurement of the freezing points. For 2,2-dimethylhexane the quantity was so small as to make impracticable the isolation of a sample of high purity, and the amount of 2,2-dimethylhexane in its best lot from petroleum was estimated from its values of refractive index and density as compared with those of pure 2,2-dimethylhexane and the probable contaminants, as made evident from the results of the analytical distillation (see fig. 1).

The best lots from petroleum of ethylcyclopentane and 1,1,3-trimethylcyclopentane and the second-best lot of 2,2-dimethylhexane were also examined spectrographically with an infrared spectrometer [4] by the Socony-Vacuum Laboratories, using the appropriate NBS Standard Samples of hydrocarbons for calibration.

The relative amounts of the three compounds in the Ponca, Okla., petroleum are taken from the

[4] A description of this instrument is given in reference [11].

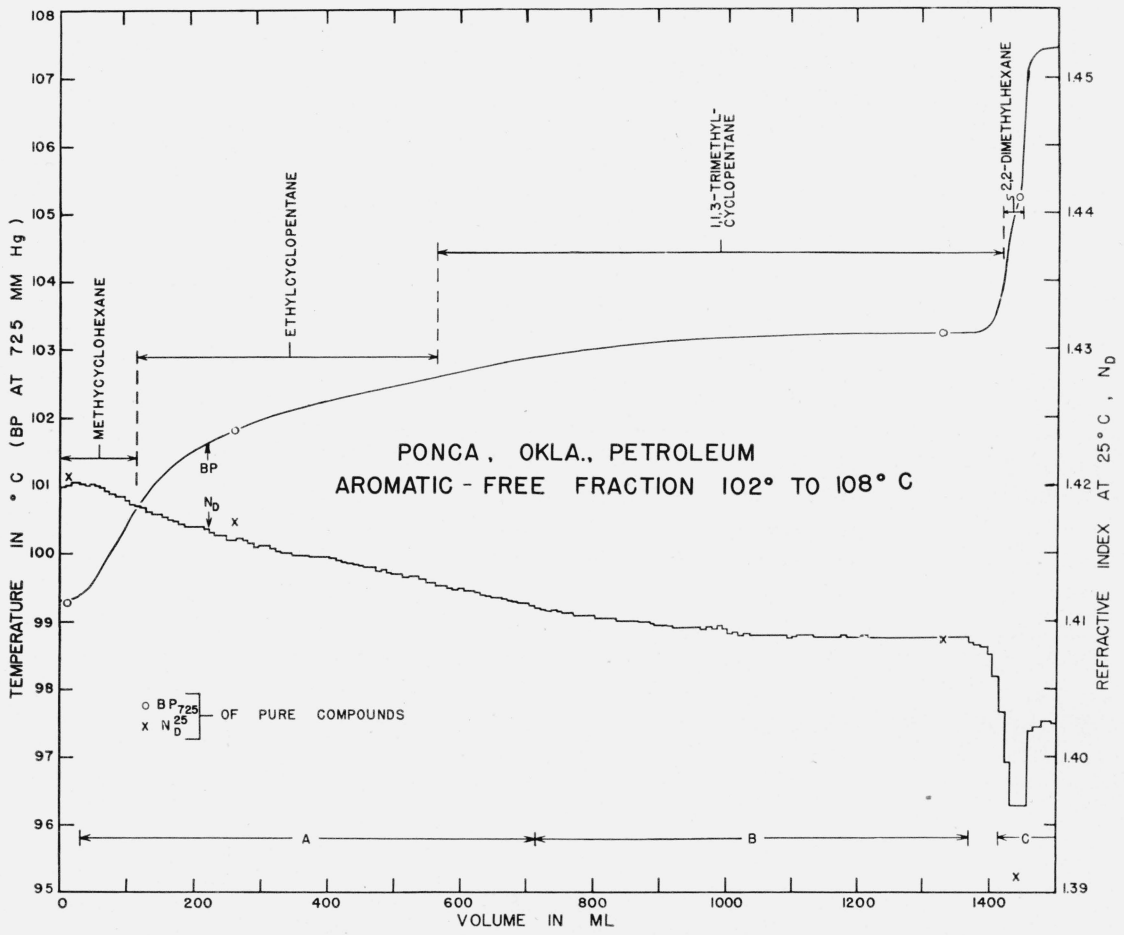


FIGURE 1.—*Distillation of the 102° to 108° C (aromatic-free) fraction of petroleum.*

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. The scale of abscissas gives the volume of distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

results of the distillation shown in figure 1. The translation of these amounts into amounts based on the entire gasoline fraction, 40° to 180° C, and on the original crude petroleum was made from unpublished data obtained in the investigation on the hydrocarbons in the gasoline fraction of seven representative crudes, which include the Ponca, Okla., petroleum [12, 13, 14]. The data of this latter investigation [14] show that, for the Ponca, Okla., naphtha, the material normally boiling in the range 102° to 108° C constitutes, by volume, $1.4_2$ percent of the gasoline fraction, 40° to 180° C, and $0.4_7$ percent of the original crude petroleum.

## IV. Results

Table 1 lists the several distillations that were performed in this investigation and gives information concerning the distillation column, the reflux ratio, the rate of collection of distillate, the azeotrope-forming substance (if used), the volume of hydrocarbon placed in the still, the volume of each fraction of distillate, and the number of the illustration in which the results of the distillation are plotted.

TABLE 1.—*Information on the distillations for the analysis and separation of ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane from the 102° to 108° C (aromatic-free) fraction of petroleum*

| Material | Distillation | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Distilling column number | Number of theoretical plates at total reflux (approximately) | Reflux ratio (approximately) | Rate of collection of distillate | Kind of distillation | Volume of azeotrope-forming substance, if used | Volume of hydrocarbon charged | Volume of each fraction of distillate | Results plotted in figure |
| | | | | *ml/hr* | | | *ml* | *ml* | |
| 102° to 108° C (aromatic-free) fraction of petroleum. | 2 | 100 | 120/1 | 2.5 | Regular | | 1,650 | 7.5 | 1 |
| Ethylcyclopentane concentrate (part *A*, fig. 1). | 3 | 100 | 165/1 | 1.8 | Azeotropic | Ethanol, 2,000 ml | 530 | 14.0 | 2 |
| Ethylcyclopentane concentrate (part *A*, fig. 2). | 3 | 100 | 165/1 | 1.8 | Regular | | 310 | 14.0 | 3 |
| 1,1,3-Trimethylcyclopentane concentrate (part *B*, fig. 1). | 11A | 200 | 180/1 | 4.0 | Azeotropic | Isopropanol, 2,000 ml | 500 | 16 | 4 |
| 2,2-Dimethylhexane concentrate (part *C*, fig. 1). | 11A | 200 | 180/1 | 4.0 | do | Ethanol, 5,000 ml | 1,950 | 16 | 5 |

Figure 1 shows the results of the distillation of that part of the petroleum containing all of the material (aromatic-free) normally boiling in the range 102° to 108° C. The relative amounts of ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane are marked in this chart. It is possible that the relative amount of ethylcyclopentane may be somewhat low because of the preferential loss of it in the previous treatment [8], which resulted in the separation of methylcyclohexane. The relative amounts of the three compounds are given in the third column of table 2. Also given in table 2 are values representing the amount of each of the compounds in the gasoline fraction, 40° to 180° C, and the amount in the original crude petroleum [12, 13, 14].

Figure 2 gives the results of the azeotropic distillation with ethanol of the concentrate of ethylcyclopentane, taken as part A in figure 1.

TABLE 2.—*Amounts of ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane in Ponca, Okla., petroleum*

| Component | Normal boiling point | Relative amount by volume | Amount in the gasoline fraction, 40° to 180° C | Amount in the original crude petroleum |
|---|---|---|---|---|
| | °C | | *Percent by volume* | *Percent by volume* |
| Ethylcyclopentane | 103.5 | 34 | $0.4_8$ | $0.1_6$ |
| 1,1,3-Trimethylcyclopentane | 104.9 | 64 | $.9_1$ | $.3_0$ |
| 2,2-Dimethylhexane | 106.8 | 2 | .03 | .01 |
| Total | ----- | 100 | $1.4_2$ | $.4_7$ |

Figure 3 gives the results of the regular distillation of the second concentrate of ethylcyclopentane, taken as part *A* in figure 2. The best lot from petroleum of ethylcyclopentane was selected from this distillate.

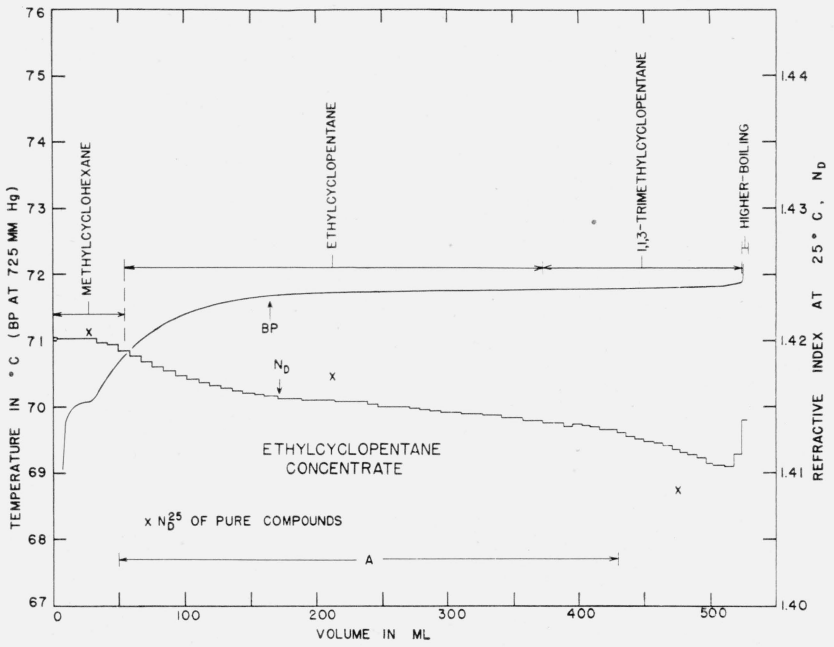


FIGURE 2.—*Distillation of the ethylcyclopentane concentrate (A, fig. 1).*

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. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

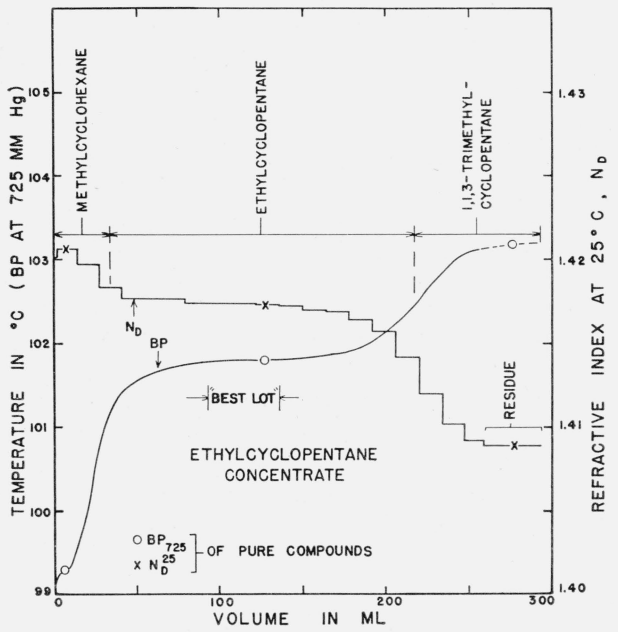


FIGURE 3.—*Distillation of the ethylcyclopentane concentrate (A, fig. 2).*

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. The scale of abscissas gives the volume of distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

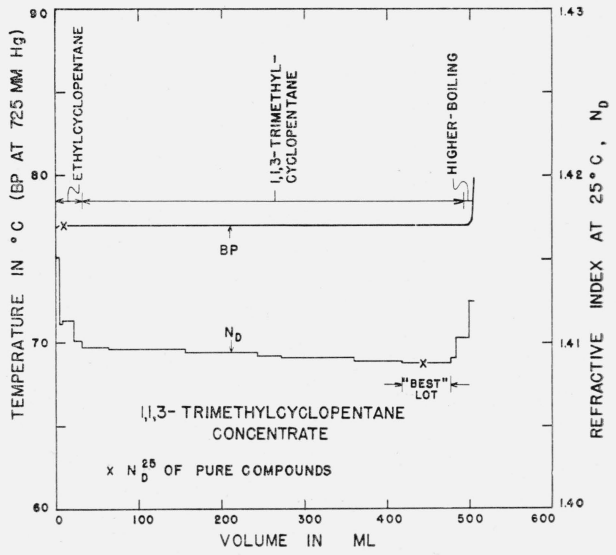


FIGURE 4.—*Distillation of the 1,1,3-trimethylcyclopentane concentrate (B, fig. 1).*

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. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

Figure 4 gives the results of the azeotropic distillation with isopropanol of the concentrate of 1,1,3-trimethylcyclopentane, taken as part B in figure 1. The best lot from petroleum of 1,1,3-trimethylcyclopentane was selected from this distillate.

Figure 5 gives the results of the azeotropic distillation with ethanol of the concentrate of 2,2-dimethylhexane. The best lot from petroleum of 2,2-dimethylhexane was taken as the small fraction *A* in figure 5. The small fraction *B* in figure 5 was used for the spectrographic analysis.

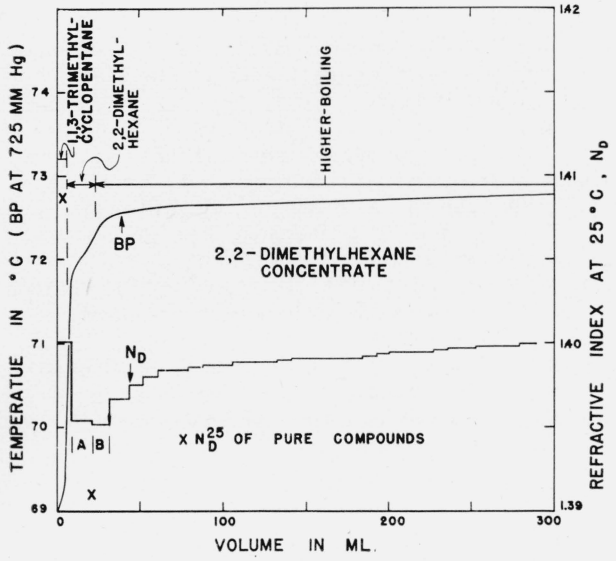


FIGURE 5.—*Distillation of the 2,2-dimethylhexane concentrate (C, fig. 1).*

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. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

The values of the simple physical properties, and the calculated purity, for the best lots from petroleum of the two alkylcyclopentanes are given in table 3. The purities of the best lots from petroleum of ethylcyclopentane and 1,1,3-trimethylcyclopentane were calculated [15] from the freezing point, and the appropriate values of the cryoscopic constant and the freezing point for zero impurity [16], to be 98.13 and 98.06 mole percent, respectively. Within the indicated limits of uncertainty, and taking cognizance of the nearly 2 percent of impurity, the values of the simple physical properties of these samples from petroleum are in accord with the corresponding values for the API–NBS samples of the same compounds [17]. Both of the best lots from petroleum of these two compounds were analyzed spectrographically with an infrared spectometer by the Socony-Vacuum Laboratories [19], with the following results for the purity, in mole percent: Ethylcyclopentane, 98.5 ± 0.8; 1,1,3-trimethylcyclopentane, 99.0 ±0.8. These results are, within the respective limits of uncertainty, in good agreement with the values calculated from the measurements of freezing points.

TABLE 3.—*Values of the simple physical properties, and the calculated purity, for the "best lots from petroleum" of ethylcyclopentane and 1,1,3-trimethylcyclopentane*

| Properties | Best lot from petroleum of ethylcyclopentane | Best lot from petroleum of 1,1,3-trimethylcyclopentane |
|---|---|---|
| Boiling point, at 760 mm, in ° C. | 103.50 ±0.05 | 104.93 ±0.05. |
| Refractive index, $N_D$, at 25° C. | 1.4174 ±0.0001 | 1.4088 ±0.0001. |
| Density,[a] in air at 1 atm, at 25° C, in g/ml. | 0.7619 ±0.0001 | 0.7442 ±0.0001. |
| Freezing point,[b] in air at 1 atm, in ° C. | −139.06 ±0.02 | −142.93 ±0.02. |
| Calculated purity,[c] mole percent. | 98.13 ±0.15 | 98.06 ±0.35. |

[a] Determined by A. F. Forziati with the apparatus described in reference [18].

[b] Determined by N. C. Krouskop, as described in reference [15].

[c] Calculated, as described in reference [15], from the value of the freezing point for zero impurity and the cryoscopic constant taken from reference [16].

Material *A* in figure 5 was selected, from the values of boiling point and refractive index, as the best lot from petroleum of 2,2-dimethylhexane. This lot, which was obviously not pure 2,2-dimethylhexane, had the following properties: Boiling point at 760 mm, 106.6±0.3° C; density at 25° C, 0.7045 g/ml; refractive index, $n_D$, at 25° C, 1.3954. The amount of 2,2-dimethylhexane in this lot was calculated to be 50 ±10 percent, from calculations made in three ways: (1) from the temperature-volume distillation data, (2) from the values of refractive index of the sample, of pure 2,2-dimethylhexane, and of the lower and higher-boiling components, and (3) from the values of refractivity intercept of the sample, of pure 2,2-dimethylhexane, and of the lower and higher-boiling components. A second and less pure lot of 2,2-dimethylhexane, *B* in

figure 5, was analyzed spectrographically with an infrared spectrometer [19] by the Socony-Vacuum Laboratories and found to contain somewhat over 20 percent of 2,2-dimethylhexane.[5]

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Grateful acknowledgment is made to P. V. Keyser, Jr., and F. P. Hochgesang, Socony-Vacuum Laboratories, Paulsboro, N. J., for the spectrographic measurements reported in this paper.

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WASHINGTON, January 24, 1947.