

Separation of the 177° to 200° C Fraction of Petroleum and the Isolation of Normal Undecane^{1 2}

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This report describes the separation of the 177° to 200° C fraction of petroleum (Ponca, Okla., crude) by means of regular distillation, azeotropic distillation, adsorption, and crystallization. A regular distillation at high efficiency with high reflux ratio separated the original petroleum into a series of substantially constant-boiling fractions. Appropriate blends of material of nearly the same boiling point were subjected to azeotropic distillation to produce a separation of the aromatic hydrocarbons from the paraffinic and cycloparaffinic hydrocarbons, with a partial separation of the latter two classes from each other. The fractions intermediate between the aromatic hydrocarbons and the paraffins plus cycloparaffins were further processed by adsorption to separate all the aromatic hydrocarbons. The azeotropic distillation yielded fractions very rich in normal undecane, and from these a pure sample of normal undecane was separated by crystallization.

I. Introduction

In continuation of the work of the American Petroleum Institute Research Project 6 on the fractionation and analysis of hydrocarbons in a large quantity of one representative petroleum [1],⁴ work was begun several years ago on the 177° to 200° C fraction of the Project's Ponca, Oklahoma, petroleum. This report describes the separation of the 177° to 200° C fraction of this original petroleum by regular distillation, azeotropic distillation, and adsorption into a portion containing all the aromatic hydrocarbons and a portion containing all the paraffinic and cycloparaffinic hydrocarbons, together with the isolation of pure normal undecane by crystallization from the hydrocarbon part of the azeotropic distillate.

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

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⁴ Figures in brackets indicate the literature references at the end of this paper.

II. Material Investigated

The material investigated consisted of all of the original petroleum (Ponca, Okla., crude) normally boiling between 177° and 200° C. A complete description of the original crude petroleum is given in reference [2]. The last work on the material normally boiling just below 177° C and that just above 200° C is described in references [3] and [4], respectively.

III. Apparatus and Procedure

The percentage of aromatic hydrocarbons in the entire material normally boiling in the range 177° to 200° C was determined in an analytical adsorption experiment with 1-butanol as the desorbing liquid, in accordance with the standard procedures developed in the Thermochemistry and Hydrocarbon Section at this Bureau [7, 8].

The apparatus used and the procedure followed in carrying on the fractionating processes are described in detail in the following previous publications from this section: Regular and azeotropic distillation [5], adsorption [6, 7, 8], crystallization [9].

The regular distillation of the entire material normally boiling in the range 177° to 200° C was performed in columns 5 and 6 described in reference [5], at a pressure of 725 mm Hg and with a reflux ratio of about 125 to 1. The entire material had a volume of 86.5 liters and was distilled in six charges of approximately equal volume.

The charges for azeotropic distillation were prepared by recombining material, which on the average had distilled within a range of 0.7° C during the regular distillations. Each of the 31 charges distilled azeotropically contained approximately 2.8 liters of hydrocarbons. These distillations were performed in columns 7, 8, and 13 described in reference [5], at a pressure of 725 mm Hg and with a reflux ratio of 130 to 1. The distillation of each charge was discontinued when the boiling point of the distillate and the refractive index of the hydrocarbon portion of the distillate had risen to values indicative of the absence of paraffins and cycloparaffins from the material remaining in the still.

The azeotropic distillation of the material normally boiling in the range 177° to 189° C was performed with butyl Cellosolve (ethylene glycol monobutyl ether) as the azeotrope-forming substance (see fig. 1). Over this range, the amount of hydrocarbon material in the distillate decreased roughly linearly with boiling point from 52 to 35 percent. For the material normally boiling above 189° C, methyl Carbitol (diethylene glycol monomethyl ether) was used as the azeotrope-forming substance. With methyl Carbitol, the amount of hydrocarbon material in the distillate decreased from 65 percent for material normally boiling at 189° C to 55 percent for material normally boiling at 200° C.

The hydrocarbon material in the fractions of the azeotropic distillate between the paraffins plus cycloparaffins and the aromatics was further resolved into two portions of these types by adsorption with silica gel in columns 2 cm in diameter and 7.9 meters in length. For these adsorption experiments, 1-butanol was used as the desorbing liquid.

The residue portion from each of the six regular distillations was separated in a manner similar to the foregoing, except that tert-amyl alcohol was used as the desorbing liquid. Intermediate frac-

tions from the adsorption process were reprocessed until the volume of the remaining intermediate portion became negligible.

Normal undecane (see section V) was separated from appropriate fractions by repeated crystallization with centrifuging [9], at -40° C, using a 2 to 1 mixture of hydrocarbon material with acetone. Final purification of the normal undecane was effected by adsorption [6].

IV. Results of the Fractionation

1. Regular Distillation

The results of the regular distillation of one of the six identical charges are shown in figure 1. Of the total of 86.5 liters of material distilled, 0.7 liter was material normally boiling below 177° C, and 7.0 liters was material normally boiling above 200° C. The curve of the refractive index of the distillate in figure 1 shows, near 187° and 194° C, two pronounced dips due to high concentrations of paraffinic hydrocarbons. These dips are attributable, respectively, to concentrates of methyldecanes and of normal undecane. Beneath the plot of refractive index for the fractions of distillate, there is a similar plot for the aromatic-free portion of each of these same fractions.⁵ The difference between these plots is represented at the top of the figure by the curve labeled Δn_D , and indicates in a general way the distribution of aromatic hydrocarbons throughout the distillate. A better picture of the distribution of aromatics is shown, however, by the curve giving the actual percentage of aromatic hydrocarbons by volume. This latter is based upon the measured volume of aromatic material recovered from the individual azeotropic distillations and adsorptions. A correction for losses was uniformly applied throughout the boiling range, upon the basis of the results of the analytical adsorption on the entire material.

2. Azeotropic Distillation

The results of the azeotropic distillation are shown for three charges (A, B, and C; see fig. 1) in figure 2. The sharp increase in refractive index

⁵ The refractive index for the aromatic-free portion (paraffins and cycloparaffins) of each fraction was obtained by passing 1 ml through a small column of silica gel (200 mm in length and 2 mm in inside diameter). The first drop of filtrate was used to determine the refractive index. See reference [10].

immediately preceding the end of the distillation to values characteristic of aromatic hydrocarbons is apparent for all three charges, and shows that the azeotropic distillation was satisfactorily separating the aromatic hydrocarbons from the paraffins and cycloparaffins. For the nonaromatic portion of any one charge, there are marked variations in refractive index, a consequence of a partial separation of paraffins from cycloparaffins. This separation did not take place among the various distillations in the uniform manner shown by charge A. Thus, with charge B there were two depressions in the refractive index curve before the final sharp increase. With charge C, which was rich in normal undecane, the central portion of the distillate had a refractive index only 0.003 higher than that of pure normal undecane. Flanking each side of the region rich in normal undecane there was material with a higher refractive index, which contained cycloparaffins and possibly bicycloparaffins. It is, in fact, apparent for charge C that a bicycloparaffin was concentrated in the fractions that immediately preceded the appearance of aromatic material in the distillate.

3. Adsorption

The results of the analytical adsorption experiment on the entire material are shown in figure 3, from which the aromatic content of the entire distillate was calculated to be 16.1 ± 0.2 percent by volume. The total volume of aromatic hydrocarbons separated by azeotropic distillation and by adsorption was 13.0 liters, of which 1.7 liters originally distilled outside of the normal boiling range, 177° to 200° C (175.3° to 198.3° C at 725 mm Hg). For the portion of the distillate normally boiling between 177° and 200° C, the percentage of aromatic hydrocarbons was calculated to be 15.3 percent by volume.

The results of a typical adsorption experiment are shown in figure 4. It will be observed that a satisfactory separation of paraffins and cycloparaffins from aromatic hydrocarbons was obtained.

V. Isolation of Normal Undecane

The concentrate of normal undecane produced by the azeotropic distillation was used as the starting material for the isolation of a small (50 ml) sample of substantially pure normal undecane. About 0.9 liter of material with a refractive index, n_D^{25} , of 1.4177 was crystallized as described in section III, yielding approximately 0.3 liter of material with a refractive index of 1.4153. The normal undecane thereby separated was further fractionated by adsorption, as described in section III, and the results of this fractionation are shown in figure 5. The fraction with the lowest refractive index, indicated as A in figure 5, was taken as the best sample from this processing. Values for certain physical properties of this sample are as follows:⁶ boiling point at 760 mm Hg, 195.893° C; density at 25° C, 0.73662 g/ml; refractive index, n_D^{25} , 1.41507; specific dispersion, $(n_F - n_C)/d$ at 25° C, 0.00979; freezing point in air at 1 atm, -25.678° C; calculated purity, 99.7 mole percent.

No attempt was made to prepare a sample of the highest purity in the course of this investigation, since normal undecane is being prepared as an API-Standard and API-NBS hydrocarbon [15].

VI. Conclusion

The foregoing describes the separation of the entire 177° to 200° C fraction of the original crude petroleum (Ponca, Okla.) into an aromatic portion and a portion containing the paraffins and cycloparaffins, together with a partial separation of cycloparaffins from paraffins and the isolation of normal undecane from the latter. The next work on the 177° to 200° C fraction of this petroleum will include the isolation of individual compounds from the aromatic portion, the complete separation of the cycloparaffins from the paraffins, and the separation of individual compounds from the latter two portions.

⁶ The boiling point, density, and refractive index were determined by A. F. Forziati [11, 12, 13]. The determination of the freezing point and purity was made by L. F. Soule under supervision of A. J. Streiff [14, 15].

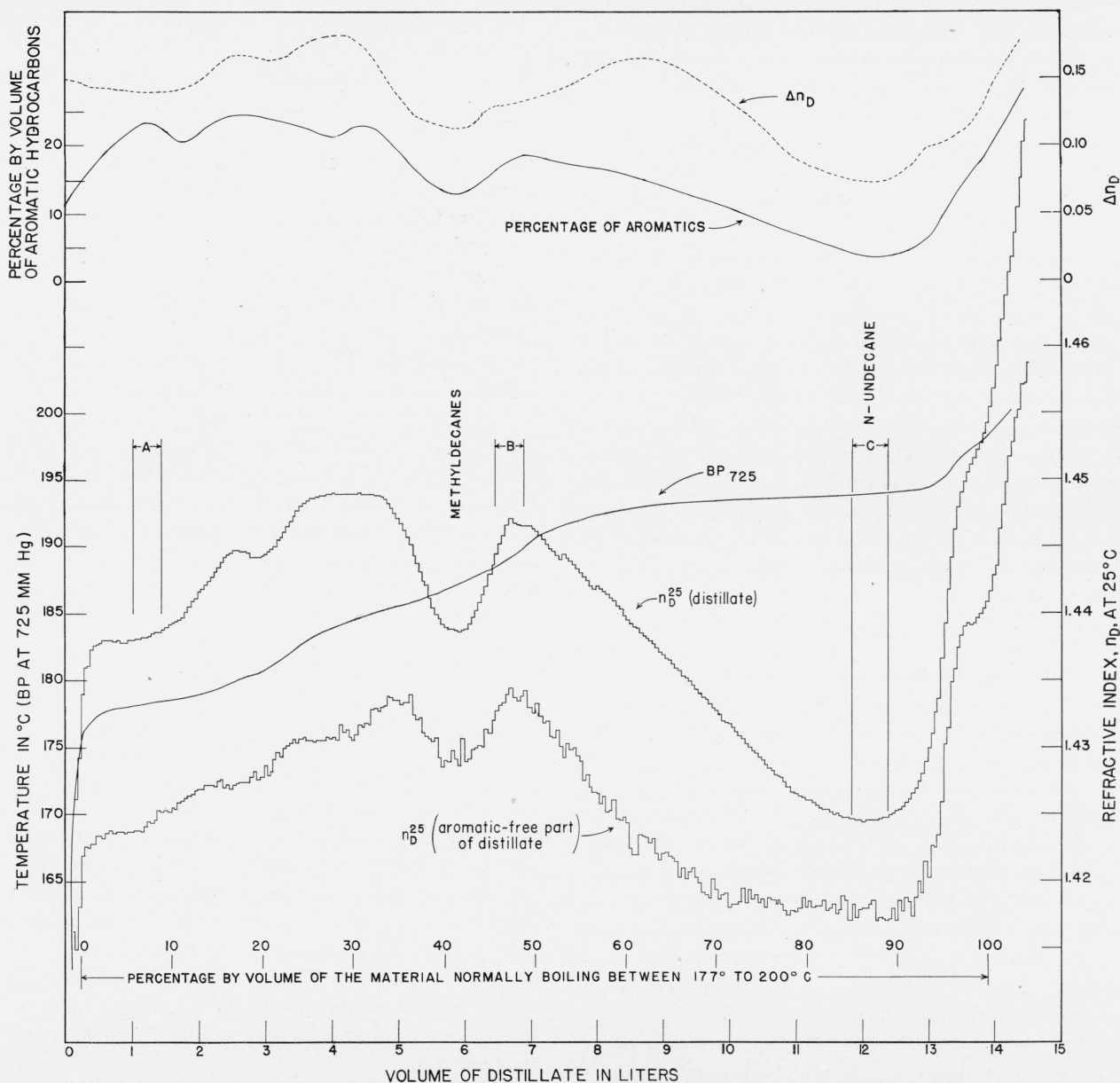


FIGURE 1. Regular distillation of the 177° to 200° C fraction of petroleum.

The lower scale of ordinates on the right gives the refractive indices of the fractions of the distillate as obtained and on an aromatic-free basis (see footnote 3). The lower scale of ordinates on the left gives the boiling point of the distillate at a pressure of 725 mm Hg. The upper scale of ordinates on the right gives the difference in refractive index for the two lowermost plots. The upper scale of ordinates on the left gives the percentage of aromatic hydrocarbons by volume. The scale of abscissas gives the volume of the distillate in milliliters. The results of the azeotropic distillation of the portions designated A, B, and C are given in figure 2.

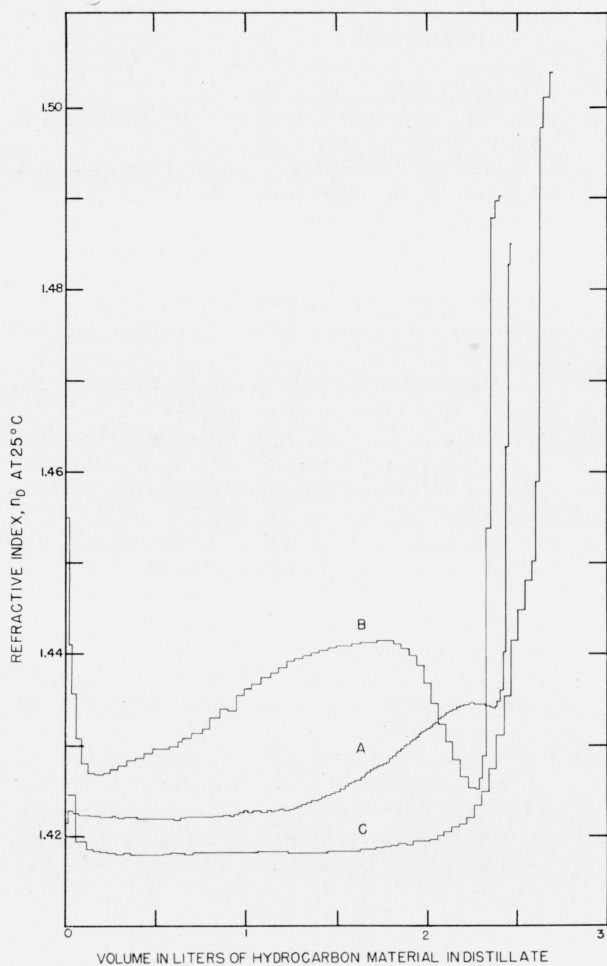


FIGURE 2. Azeotropic distillation of three representative portions of the 177° to 200° C fraction of petroleum.

The scale of ordinates gives the refractive index of the hydrocarbon material in the fractions of azeotropic distillate, and the scale of abscissas gives the volume in milliliters of the hydrocarbon material in the distillate. The letters A, B, and C refer to the three charges indicated in figure 1.

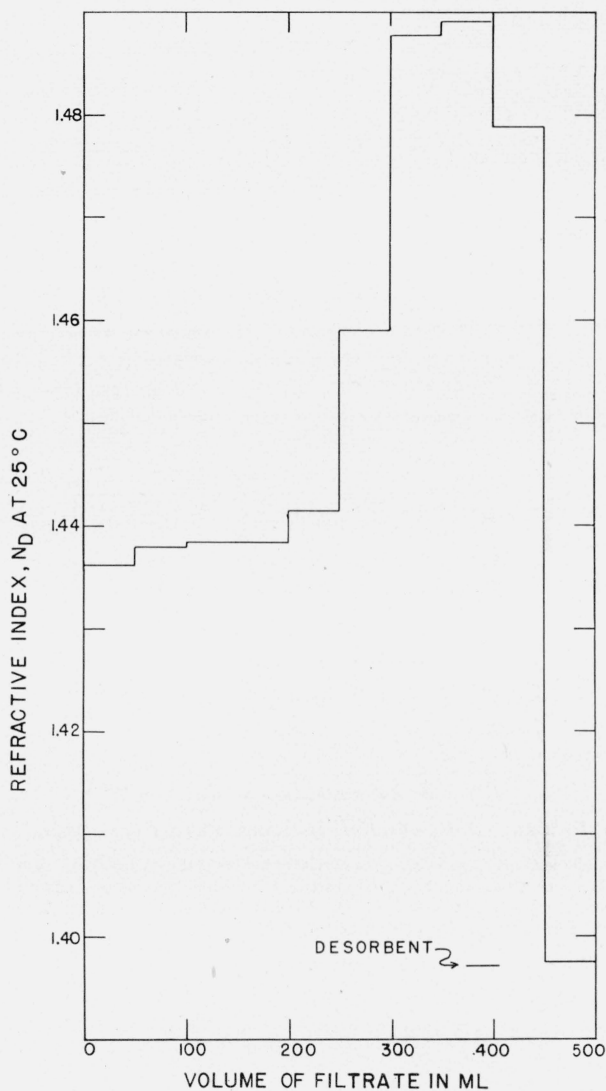


FIGURE 3. Adsorption of the mixture of paraffins, cycloparaffins, and aromatic hydrocarbons remaining from the azeotropic distillations of the 177° to 200° C fraction of petroleum.

The scale of ordinates gives the refractive indices of the fractions of the filtrate and scale of abscissas the volume of the filtrate in milliliters.

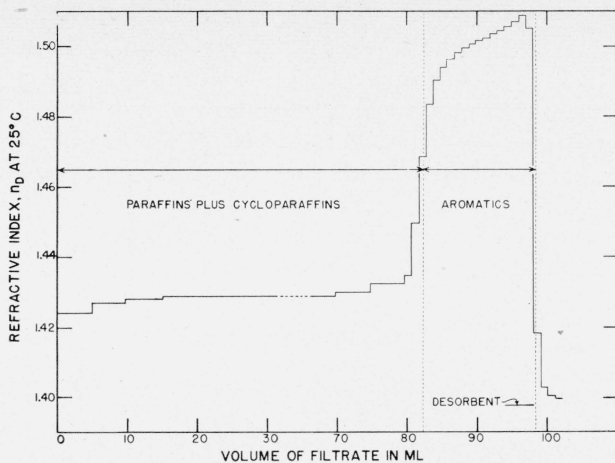


FIGURE 4. Analytical adsorption experiment on the original 177° to 200° C fraction of petroleum.

The scale of ordinates gives the refractive indices of the fractions of the filtrate and scale of abscissas the volume of the filtrate in milliliters.

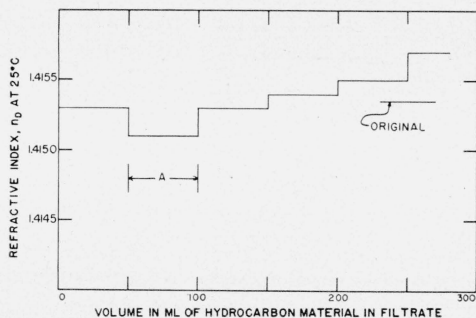


FIGURE 5. Purification of *n*-undecane by adsorption.

The scale of ordinates gives the refractive indices of the hydrocarbon material in the filtrate and the scale of abscissas the volume in milliliters of hydrocarbon material in the filtrate. The portion designated by the letter A was taken as the best sample from this processing.

VII. References

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