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SUMMARY OF AN INVESTIGATION OF THE COMPOSITION OF A MIDCONTINENT PETROLEUM DISTILLATE, BOILING BETWEEN 100° AND 130° C. [1]

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ABSTRACT

The results of 7 years of investigation of the composition of the naphtha fraction of petroleum boiling between 100° and 130° C are summarized. Of the 130 liters found to boil in this range after the first laboratory distillation, the constituents of about one-sixth of the volume were identified or characterized by physical properties, isolated or concentrated, and their concentration in the petroleum roughly estimated. About one-fourth of the volume remains as unidentified distillate. This is composed in part of material of which the constitution is only predicted (about one-twelfth of the volume) and of additional quantities of the constituents which were isolated previously (about one-sixth of the volume). The remainder was lost during the investigation or distilled out of the range on subsequent distillations. Photomicrographic studies were made of those concentrations of distillate which could be crystallized. There is given a bibliography of the physical constants of hydrocarbons reported to boil within this range.

CONTENTS

I. INTRODUCTION

This paper summarizes the work done to date since 1929 with the portion of midcontinent petroleum distilling between 100° and 130° C and includes some new information obtained since the publication of a previous summary paper [3] and two subsequent specialized papers.[4 5]

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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[3] R. T. Leslie and J. D. White, J. Research NBS **15**, 211 (1935) RP824.

[4] R. T. Leslie, J. Research NBS **17**, 761 (1936) RP943.

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About 6 percent of the total volume of the crude petroleum distilled between 100° and 130° C and, of this, by far the largest volume distilled between 117° and 128° C. Curves A_1 and A_2 of figure 1 show, respectively, the refractive indices and the distribution of volumes after four distillations in the laboratory, before the removal of any of the constituents. Curves B_1 and B_2 of the same figure show the distillate still remaining after the removal of seven hydrocarbons and the distillation of the residual material. This is composed of the unidentified constituents and of unisolated residues of the identified compounds. Although unidentified constituents which boil chiefly between 101.5° and 116° C still remain, the constituents present in the largest proportions have been removed. The paper includes, besides a summary of the compounds actually isolated, all the information concerning the material represented by curves B_1 and B_2 of figure 1. In addition, the values of physical constants for the hydrocarbons reported in the literature to boil within the range are given in table 1. This information was obtained by surveying the literature up to 1937, including standard works of reference. The values were selected from publications dealing with the preparation of pure compounds or apparently reliable measurements of the properties of nearly pure compounds. Where necessary, the only available data were included. The best values, in the author's opinion, have been plotted in figure 1, and are numbered for convenient reference to the table.[6]

[6] Figures in brackets throughout the paper are the reference numbers given in figure 1 and table 1.

TABLE 1.—*Properties of known paraffinic, naphthenic, and aromatic hydrocarbons boiling between 98° and 130° C.*

(Compounds are arranged in order of increasing boiling points)

Reference number	Normal boiling point	Freezing point	Specific gravity	Refractive index	Heat of fusion	Literature references
			n-Heptane			
	°C	°C	d_4^{20}	n_D^{20}	cal/g	
1	98.4	−90.5	0.6836	1.38777		G. Edgar, G. Calingaert, and R. E. Marker, J. Am. Chem. Soc. **51**, 1483 (1929).
	98.38	−90.65	.68378	1.38775		A. F. Shepard, A. L. Henne, and T. Midgley, Jr., J. Am. Chem. Soc. **53**, 1948 (1931).
	98.38	−90.62		1.38510^{25}		B. J. Mair, BS J. Research **9**, 457 (1932) RP482.
		−90.9			33.78	H. M. Huffman, G. S. Parks, and S. B. Thomas, J. Am. Chem. Soc. **52**, 3241 (1930).
	98.36_5					M. Wojciechowski, J. Research NBS **17**, 453 (1936) RP921.
	98.41_3					E. R. Smith and H. Matheson, J. Research NBS **20**, 641 (1938) RP1097.
			2,2,4-Trimethylpentane			
2	99.3		0.6914_{20}^{20}	1.3921		G. Edgar, Ind. Eng. Chem. **19**, 145 (1927).
		−107.8			2160 cal/mole	G. S. Parks and H. M. Huffman, Ind. Eng. Chem. **23**, 1138 (1931).
		−107.41				J. H. Bruun and M. M. Hicks-Bruun, BS J. Research **9**, 269 (1932).
	99.3		.6918	1.3916		K. C. Laughlin and F. C. Whitmore, J. Am. Chem. Soc. **55**, 2608 (1933).
	99.23_4					E. R. Smith and H. Matheson, J. Research NBS **20**, 641 (1938) RP1097.
			Methylcyclohexane			
3	101.20	−126.4	0.77340^{15}	1.42535^{15}		J. Timmermans and F. Martin, J. chim. phys. **23**. 747 (1926).
	99.8 to 100.8		$.769_{20}^{20}$	1.4230		F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55**, 3326 (1933).
	101.0 ±0.5		.7696	1.4239		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18**, 751 (1932).
		−126.85				J. Timmermans, Comm. Phys. Lab. Univ. Leiden, Suppl. **64**, 3 (1929).
		−126.9			16.24	G. S. Parks and H. M. Huffman, J. Am. Chem. Soc. **52**, 4385 (1930).
	102.8		.7963	1.4232		E. C. Bromiley and D. Quiggle, Ind. Eng. Chem. **25**, 1136 (1933).

TABLE 1.—*Properties of known paraffinic, naphthenic, and aromatic hydrocarbons boiling between 98° and 130° C.*—Continued

Reference number	Normal boiling point	Freezing point	Specific gravity	Refractive index	Heat of fusion	Literature references
			Ethylcyclopentane			
	°C	°C	d_4^{20}	n_D^{20}	cal/g	
4	103.0 ±0.5		0.7695	$1.4201^{20.4}$		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18**, 751 (1932).
		−137.9				J. Timmermans, Bul. soc. chim. Belg. **36**, 502 (1927).
			1,1,2-Trimethyl-2-ethylcyclopropane			
5	103.5 to 104.5		$0.7418^{20.4}$	1.4129		R. Lespieau and R. Wakeman, Bul. soc. chim. **51**, 392 (1932). (Only 1 ml of product.)
			1,2-Dimethyl-1-ethylcyclopropane			
6	104		0.7418	1.4129		R. Lespieau and R. Wakeman, Bul. soc. chim. **51**, 399 (1932).
			2, 2, 3, 3-Tetramethylbutane			
7	106 to 107	+103 to 104				A. Richard, Ann. chim. phys. [8] **21**, 357 (1910).
	106 to 107 [765]	+103 to 104				L. Henry, Compt. rend. **142**, 1075 (1906).
	104 to 105.2	+100.7 to 101.4				D. T. Flood and G. Calingaert, J. Am. Chem. Soc. **56**, 1211 (1934).
		+104			14.9	G. S. Parks and H. M. Huffman, Ind. Eng. Chem. **23**, 1138 (1931).
			2, 2,-Dimethylhexane			
8	106 to 107		0.6967	1.3931		C. R. Noller, J. Am. Chem. Soc. **51**, 594 (1929).

			2, 5-Dimethylhexane			
9	107 ^{747}		0.6937 $^{20}_{20}$	1.3922		M. Tuot, Compt. rend. **197**, 1434 (1933).
	108.25		.6991 $^{15}_{15}$	1.3930 ^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
	109.2 ±0.1		.6986 $^{20}_{20}$	1.3932		H. Graef, Bul. soc. chim. Belg. **40**, 315 (1931).
			1-Methyl-1, 2-diethylcyclopropane			
10	108 to 109		0.7382 $^{20}_{0}$	1.4102		N. Kishner, J, Russ. Phys. Chem. Soc. **44**, 179; Chem. Zentr. **1912** I, 2025 (listed in Beilsteins Ergänzungsband 4th ed, **5**). Also listed by R. Lespieau and R. Wakeman, Bul. soc. chim. **51**, 399 (1932).
			2, 4-Dimethylhexane			
11	108 ^{750}		0.6986 $^{20}_{20}$	1.3950		M. Tuot, Compt. rend. **197**, 1434 (1933).
	110.0 ^{763}		.7083 $^{15}_{15}$	1.3986 ^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
	110 to 111		.703 $^{21}_{4}$			P. A. Levene and R. E. Marker, J. Biol. Chem. **91**, 405 (1931).
			1-Methyl-2-isobutylcyclopropane			
12	109.5 to 110.5		0.7403	1.4088		N. D. Zelinsky and A. E. Upenski, J. Russ. Phys. Chem. Soc. **45**, 839; Ber. deut. Chem. Ges. **46**, 1472 (1913) (Listed in Beilsteins Ergänzungsband 4th ed., 5). Also listed by R. Lespieau and R. Wakeman, Bul. soc. chim. **51**, 399 (1932).
			Toluene			
13	110.614			1.4961		W. Świetosławski, Ann. acad. sci. tech. Varsovíe, **3**, 28 (1936).
	110.4 ±0.2		0.8652	1.4947		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18**, 751 (1932).
	110.80	−95	.87160 ^{15}	1.49985 ^{15}		J. Timmermans and F. Martin, J. chim. phys. **23**, 747 (1926).
					90.5	M. Schmitt, Compt. rend. **199**, 1299 (1934).
			2, 2, 3-Trimethylpentane			
14	110.5 to 110.8		0.7219 $^{15}_{15}$	1.4164 ^{25}		L. Clarke and W. N. Jones, J. Am. Chem. Soc. **34**, 174 (1912).
	110.2 (Cottrell)		.7173	1.4030		K. C. Laughlin and F. C. Whitmore, J. Am. Chem. Soc. **55**, 2608 (1933).

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TABLE 1.—*Properties of known paraffinic, naphthenic, and aromatic hydrocarbons boiling between 98° and 130° C.*—Continued

Reference number	Normal boiling point	Freezing point	Specific gravity	Refractive index	Heat of fusion	Literature references
			Dextro-3, 5-dimethylhexane (α_D^{30}+2.99)			
	°C	°C	d_4^{20}	n_D^{30}	cal/g	
15	111 to 112		0.696 $^{30}_{4}$			P. A. Levene and R. E. Marker, J. Biol. Chem. **95**, 23 (1932).
			3, 3-Dimethylhexane			
16	111 to 112		0.7116	1.3998		C. R. Noller, J. Am. Chem. Soc. **51**, 594 (1929).
			1,2,3-Trimethylcyclopentane			
17	111.5 to 114 114 to 115		0.7688 ^{19}	1.42591 1.4230 ^{19}		A. W. Crossley and N. Renouf, J. Chem. Soc. **89**, 27, 40 (1906). N. D. Zelinsky and N. Lepeschkin, J. Russ. Phys. Chem. Soc. **33**, 549 (1902); Chem. Zentr. **1902**, I, 33. (Listed in Beilsteins Handbuch 4th ed., 5.)
			2,3,4-Trimethylpentane			
18	112.8		0.7197	1.4045		K. C. Laughlin and F. C. Whitmore, J. Am. Chem. Soc. **55**, 2608 (1933).
			1,2,4-Trimethylcyclopentane			
19	112.5 to 113		0.7565	1.4156		N. D. Zelinsky, J. Russ. Phys. Chem. Soc. **35**, 565. (Listed in Beilsteins Ergänzungsband, 4th ed. 5.)
			2,3,3-Trimethylpentane			
20	113.6		0.7258	1.4074		K. C. Laughlin and F. C. Whitmore, J. Am. Chem. Soc. **55**, 2608 (1933).

			2,3-Dimethylhexane			
21	113.9		0.7246^{15}_{15}	1.4075^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
			2-Methyl-3-ethylpentane			
22	114		0.7084^{15}	1.3996^{25}		L. Clarke Am. Chem. J. **39**, 578 (1908). Reported in Beilsteins Handbuch, 3d ed., **1**.
			1,1,2-Trimethylcyclopentane			
23	113 to 114^{749}		0.7661^{20}_{0}	1.4199		N. Kishner, J. Russ. Phys. Chem. Soc. **42**, 1211; Chem. Zentr. **1911**, I, 543. (Listed in Beilsteins Ergänzungsband, 4th ed., **5**.)
			1,1,3-Trimethylcyclopentane			
24	115 to 116		0.7703	1.4223		N. D. Zelinsky and A. E. Upenski, J. Russ. Phys. Chem. Soc. **45**, 839; Ber. deut. chem. Ges. **46**, 1472 (1913). (Listed in Beilsteins Ergänzungsband, 4th ed., **5**.)
			3,3-Dimethylbicyclo-(0,1,3) hexane			
25	115		0.7962	1.4331		N. D. Zelinsky and A. E. Upenski, J. Russ. Phys. Chem. Soc. **45**, 839; Ber. deut. chem. Ges. **46**, 1466 (1923). (Listed in Beilsteins Ergänzungsband, 4th ed. **5**.)
	115.2 to 115.4		.8125	1.4385		A. E. Upensky, J. Russ. Phys. Chem. Soc. **51**, 259; Chem. Zentr. **1923**, III, 757.
			2-Methylheptane			
26	116		0.7035^{15}_{15}	1.3944^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
	117.2	−111.3	$.7035^{20}_{20}$	1.3949	2,200 cal/g mole	R. T. Leslie, BS J. Research **10**, 617 (1933) RP552.

TABLE 1.—*Properties of known paraffinic, naphthenic, and aromatic hydrocarbons boiling between 98° and 130° C.*—Continued

Reference number	Normal boiling point	Freezing point	Specific gravity	Refractive index	Heat of fusion	Literature references
			3,4-Dimethylhexane			
	°C	°C	d_4^{20}	n_D^{20}	cal/g	
27	116.5		0.7270_{15}^{15}	1.4038^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
	118.7	"glassy"				J. Timmermans, Bul. soc. chim. Belg. **36**, 502 (1927).
			3-Methylheptane			
28	116.5^{746}		0.7033_{20}^{20}	1.3982		M. M. Tuot, Compt. rend. **197**, 1434 (1933).
	119.0 ± 0.05^{760}		$.7095_4^{15}$	$1.3987^{15}_{\text{red line of He}}$		H. Van Rissenghem, Bul. soc. chim. Belg. **39**, 369 (1930).
	117.6		$.7167_{15}^{15}$	1.4022^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
			3-Ethylhexane			
29	118.8 to 119^{766}		0.7175_{15}^{15}	1.3993^{25}		L. Clarke and R. Riegel, J. Am. Chem. Soc. **34**, 674 (1912).
			Cycloheptane			
30	118 to 120		0.8099	1.4440		N. A. Rosanow, J. Russ. Phys. Chem. Soc. **48**, 318; Chem. Zentr. **1924** I, 2425. (Listed in Beilsteins Ergänzungsband, 4th ed. **5**, 29).
	118^{726}	−12 to −13	.8108	1.44521		R. Willstatter and T. Kametaka, Ber. deut. chem. Ges. **41**, 1483. (Listed in Beilsteins Ergänzungsband, 4th ed. **5**, 29).
	117 to 117.3^{736}		$.8093_0^{20}$			W. Markownikow, J. Russ. Phys. Chem. Soc., **34**, 908; Chem. Zentr. **1903** I, 568. (Listed in Beilsteins Ergänzungsband, 4th ed. **5**, 29).

			4-Methylheptane			
31	118		0.7217^{15}_{15}	1.3978^{25}		L. Clarke, J. Am. Chem. Soc. **33**, 520 (1911).
			3-Methyl-3-ethylpentane			
32	118.5 to 119 [750]		0.713^{19}	1.4028^{19}		J. Tafel and W. Jurgens, Ber. deut. chem. Ges. 1909, **42**, 2548.
			trans-1, 4-Dimethylcyclohexane			
33	119.63	−37.2	0.76264	$1.42160^{18.8}_{J \text{ line of He}}$		O. Miller, Bul. soc. chim. Belg. **44**, 513 (1935).
			1,4-Dimethylcyclohexane			
33	121.7 ±1.0	−59	0.7727	1.4253		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18**, 764 (1932).
	122 to 124		$.777^{20}_{20}$	1.4271		F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55**, 3326 (1933).
			1,1-Dimethylcyclohexane			
34	119.8	−34.1	0.78073	$1.42959^{18.8}_{J \text{ line of He}}$		O. Miller, Bul. soc. chim. Belg. **44**, 513 (1935).
	119.2 to 119.7		$.7843^{16}$	1.4320^{16}		N. D. Zelinsky and A. E. Upenski, Ber. deut. chem. Ges. **46**, 1466 (1923).
			1-Methyl-3-ethylcyclopentane			
35	120.5 to 121 [756]			1.4214^{16}		N. D. Zelinsky, Ber. deut. chem. Ges. **35**, 2679 (1902).
			trans-1,3-Dimethylcyclohexane			
36	120.40	−79.4	0.76628	$1.43254^{18.8}_{J \text{ line of He}}$		O. Miller, Bul. soc. chim. Belg. **44**, 513 (1935).

TABLE 1.—*Properties of known paraffinic, naphthenic, and aromatic hydrocarbons boiling between 98° and 130° C.*—Continued

Reference number	Normal boiling point	Freezing point	Specific gravity	Refractive index	Heat of fusion	Literature references
			1,3-Dimethylcyclohexane			
	°C	°C	d_4^{20}	n_D^{20}	cal/g	
36	120.9 to 122.5		0.774_{20}^{20}	1.4253		F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55,** 3326 (1933).
	121.6 ± 1.0		.7723	1.4255		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18,** 751 (1932).
			2,2,4,4-Tetramethylpentane			
37	122.30	−66.9 to −67.1	0.7185	1.40695		Private communication from H. A. Southgate and F. C. Whitmore, Pennsylvania State College.
			2,2,5-Trimethylpentane			
38	121 to 123		0.7091	1.3997		C. R. Noller, J. Am. Chem. Soc. **51,** 594 (1929).
	126^{764}		$.7082_0^{20}$	1.3987		N. Kishner, J. Russ. Phys. Chem. Soc. **45,** 954; Chem. Zentr. **1913** II, 2130. (Listed in Beilsteins Ergänzungsband, 4th ed. **5.**
			trans-1,2-Dimethylcyclohexane			
39	123.70	−89.4	0.77601	$1.42768_{J\text{ line of He}}^{18.8}$		O. Miller, Bul. soc. chim. Belg. **44,** 513 (1935).
			1,2-Dimethylcyclohexane			
39	126.4 to 128.9		0.792_{20}^{20}	1.4332		F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55,** 3326 (1933).
	127.9 ± 1.0		.7874	1.4314		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18,** 764 (1932).
			Isopropylcyclopentane			
40	$123 \text{ to } 124^{731.6}$		0.7785^{18}	1.4273^{18}		B. A. Kazanskii, A. F. Plate, and G. M. Gnatenko, Ber. deut. chem. Ges. **69B,** 954 (1936).

1-Methyl-2-ethylcyclopentane

41	124					T. R. Marshal and W. H. Perkin, J. Chem. Soc. **57,** 250 (1890).

1,1,3,3-Tetramethyl-2,4-diethylcyclobutane

42	124 to 125					E. Wedekind and M. Miller, Ber. deut. chim. Soc. **44,** 3286 (1911).

cis-1,4-Dimethylcyclohexane

43	124.59	−91.6	0.78271	$1.43029^{18.8}_{J\text{ line of He}}$		O. Miller, Bul. soc. chim. Belg. **44,** 513 (1935).

n-Octane

44	125.59	−56.82		1.39509^{25}		B. J. Mair, BS J. Research **9,** 457 (1932) RP482.
	125.59	−56.90	0.70279	1.39760		A. F. Shepard and A. L. Henne, J. Am. Chem. Soc. **53,** 1948 (1931).
	125.65[8]					M. Wojciechowski, J. Research NBS **17,** 453 (1936) RP921.
	124.7		$.7068^{15}_{15}$	1.3963^{25}		L. Clarke, J. Am. Chem. Soc. **33,** 520 (1911).
		−57.3			43.2	G. S. Parks and H. M. Huffman, Ind. Eng. Chem. **23,** 1138 (1931).

2,3,5-Trimethylhexane

45	129^{738}		0.7171^{20}_{20}	1.4051^{20}		M. M. Tuot, Compt. rend. **197,** 1434 (1933).

cis-1,2-Dimethylcyclohexane

46	130.04	−50.1	0.79625	$1.43663^{18.8}_{J\text{ line of He}}$		O. Miller, Bul. soc. chim. Belg. **44,** 513 (1935).

n-Propylcyclopentane

47	130.6 ± 0.2		0.7766	1.4269		F. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. **18,** 761 (1932).
		−120.3				J. Timmermans, Bul. soc. chim. Belg. **36,** 502 (1927).

II. STUDY OF THE COMPOSITION OF THE DISTILLATE

1. DISTILLATE BETWEEN 98° AND 102° C

In earlier work on the portion of petroleum boiling between 60° and 100° C, a large quantity of a nearly constant-boiling mixture of *n*-heptane and methylcyclohexane was found just below 100° C. The material also contained, as did all the distillate boiling between 95° and 108° C, a considerable quantity of toluene.

Further systematic distillation, after the removal of the major portion of these constituents,[7] [8] probably resulted in the reappearance at about 98° and 102° C of the concentration shown by curve B_2 of figure 1. The maximum volume was found to distil between 100° to 100.5° C, and this coincides with the temperature at which a maximum in the refractive-index curve (1.422_D^{20}) appears. The boiling range and refractive index correspond very nearly to the properties of methylcyclohexane [3]. The photomicrographs of crystals of the material boiling at 101.2° C (fig. 1) support this conclusion.[9]

The material distilling just below this peak shows a rapidly decreasing refractive index, the minimum index (1.3925_D^{20}) occurring at 97.5° to 98° C. This indicates that the lower-boiling constituent of the large-volume fraction was chiefly a paraffin hydrocarbon. Table 1 lists two hydrocarbons, *n*-heptane [1] and 2,2,4-trimethylpentane [2], which are reported to have approximately the properties of this fraction. Comparison of photomicrographs of the crystals from the material at 98.3° C (fig. 1) with photomicrographs of pure *n*-heptane and 2,2,4-trimethylpentane show that the chief constituent was *n*-heptane.[10]

2. DISTILLATE BETWEEN 103° AND 106° C

No great effort was made to separate the constituents other than toluene from the material boiling between 102° and 106° C, because of the relatively small quantities present and because the fractions of distillate did not crystallize readily.

Curve B_2 of figure 1 shows about 4 liters of material boiling between 102.5° and 105.5° C after the toluene was removed. The fact that the refractive-index curve slopes down more gradually above 101° C than it does below that temperature indicates either the presence of one or more naphthenic hydrocarbons boiling just above methylcyclohexane, such as ethylcyclopentane [4], 1,1,2-trimethyl-2-ethylcyclopropane [5], or 1,2-dimethyl-1-ethylcyclopropane [6], or the presence of a paraffin, such as 2,2,3,3-tetramethylbutane [7] or 2,2-dimethylhexane [8], which tended to form a constant-boiling mixture with methylcyclohexane. At 105° to 105.5° C the refractive index has dropped to a value which shows that the distillate was largely paraffinic. Attempts to crystallize fractions in this range by cooling without dilution with solvents resulted in clear glasses. When a fraction distilling at 105.2° to 105.3° C was diluted with propane and poured into liquid methane, cooled by liquid nitrogen, two liquid layers appeared. These layers were separated by using a separatory funnel constructed

[7] M. M. Hicks-Bruun and J. H. Bruun, BS J. Research **8**, 525 (1932) RP432.
[8] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research **6**, 363 (1931) RP280.
[9] [10] R. T. Leslie, and W. W. Heuer, J. Research NBS **18**, 639 (1937) RP1000.

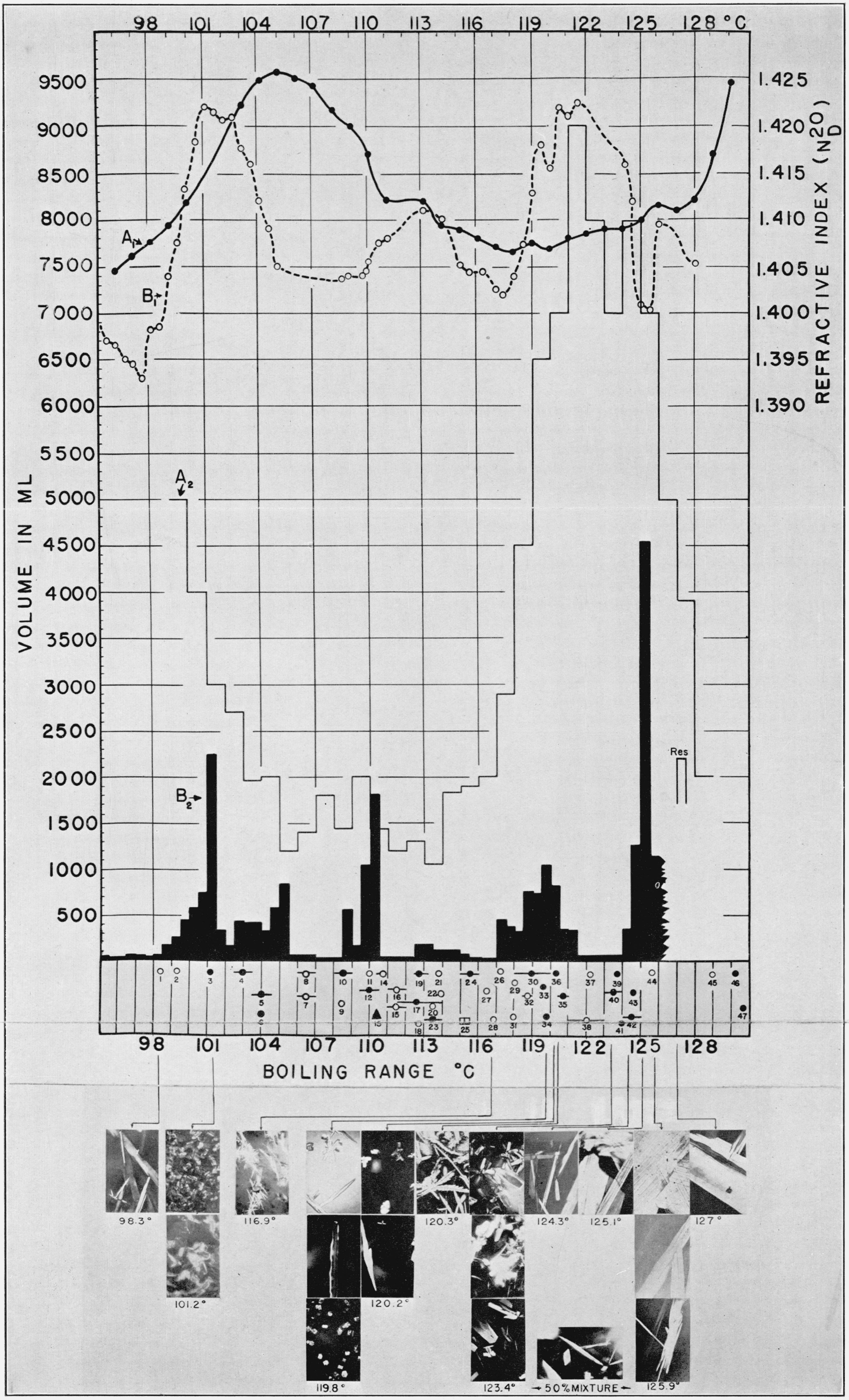

FIGURE 1.—*Volume and refractive index of fractions distilling between 95° and 130° C.*

A, status of material in 1929, after careful distillation but before removal of any constituents; *B*, status of material in 1936, after isolation or concentration and removal of seven hydrocarbons. Below the shaded graph the known hydrocarbons are indicated by the numbers referring to table 1 and the following symbols: open circles, paraffin hydrocarbons; solid disks, monocyclonaphthenes; triangle, aromatics; double square, bicyclonaphthenes; horizontal lines through circles indicate boiling range. The micrographs are of crystals from fractions of distillate; magnified about 30 times.

as shown in figure 2. The residue obtained from each layer, after boiling off the solvents, showed no difference in refractive index or the tendency to crystallize. Temperatures lower than that of liquid nitrogen might have caused crystallization of one of the layers.

From a consideration of the properties of the 5 hydrocarbons known to boil between 102° and 108° C, ethylcyclopentane [4] and 2,2-dimethylhexane [8] are most likely to occur in this small volume.

3. DISTILLATE BETWEEN 108.5° AND 110.5° C

Though the boiling point of toluene is given in the literature as about 110.8° C, very little of it was found in this fraction. The maximum concentration of the aromatic hydrocarbon was actually found to correspond with the maximum in the refractive-index curve, A_1, which occurs at about 105° C. The material represented by curve B_2 contained practically no toluene, as evidenced by the fact that the refractive index was not changed by treatment with nitrating agents or filtration through silica gel. The fact that the refractive-index curve in this range rises with boiling point indicates, therefore, that the distillate contained paraffinic mixed with higher-boiling naphthenic constituents.

When cooled, none of the fractions could be crystallized without solvents, and distillation with acetic acid failed to separate the naphthene, as shown by figure 3. Curves A_1 and A_2 of this figure show the results obtained after about 15 distillations without acetic acid in stills ranging in type of construction from 12 bubbling plates to 3-meter chain-packed columns and curves B_1 and B_2 show the results obtained after two successive fractional distillations with acetic acid. The material was distilled in three batches of about 1.5 liters each, and the distillate was again divided according to refractive index for the second distillation. It is to be observed that curves indicate very little improvement in separation.

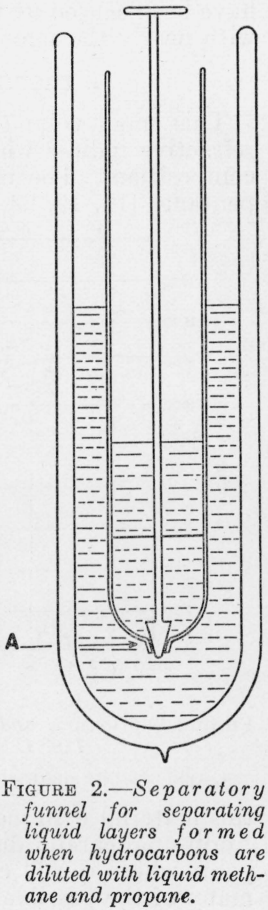

FIGURE 2.—*Separatory funnel for separating liquid layers formed when hydrocarbons are diluted with liquid methane and propane.*

A, drain orifice with ground stopper. Funnel removed from bath of liquid nitrogen to a cold test tube and lower layer drained through this opening.

Attempts to crystallize the material from methane and propane as solvents, as described above, resulted in two liquid layers, one of which was chiefly methane and the other propane, each containing petroleum hydrocarbon. The layers were separated but no differences in the properties of the fractions were observed.

The 2,5- [9], 2,4- [11], 3,3- [16], 3,5-dimethylhexanes [15], and 2,2,3-trimethylpentane [14] are shown in figure 1 as possible paraffinic constituents. The fact that the refractive-index curve rises with boiling point indicated that the naphthenic constituents were the higher-boiling components of the mixture. It appears that 1,2,3- [17], 1,1,3- [24], 1,1,2- [23], and 1,2,4-trimethylcyclopentane [19]

were the most likely possibilities, though their boiling points are higher than those of 1-methyl-1, 2-diethylcyclopropane [10] and 1-methyl-2-isobutylcyclopropane [12]. Since the total volume of material distilling between 108° and 111° C was less than 4 liters, it was estimated that the constituents of this fraction originally constituted not more than 0.1 percent of the crude petroleum. Of this, the major constituents appeared to be paraffinic. It is possible that the difficulty in separating the constituents sufficiently to obtain crystals may have been caused by the presence of a number of the isomeric octanes with nearly the same boiling points.

4. DISTILLATE BETWEEN 112° AND 116° C

This small volume of distillate, less than a liter, had a range of refractive indices which indicated that it was chiefly naphthenic in composition. The most likely constituents are the trimethylcyclopentanes [17, 19, 23, 24] mentioned above. Attempts to crystallize

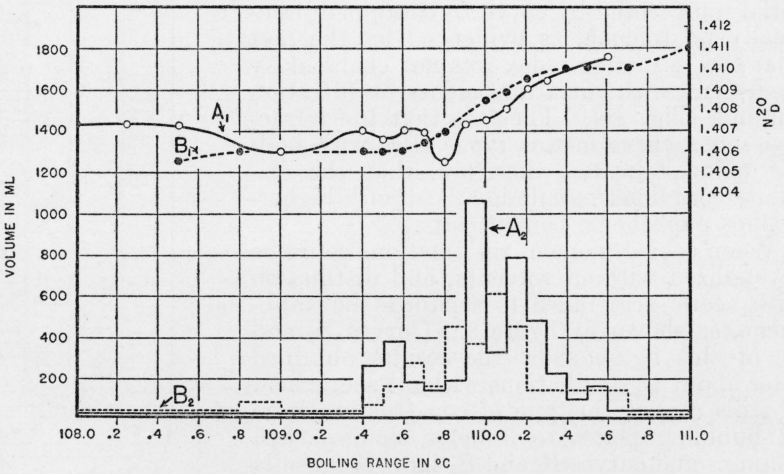

FIGURE 3.—*Volume and refractive index of material distilling between 108° and 110° C before and after distillation with acetic acid.*

A, April 1935, before distillation with acetic acid; *B*, December 1935, after distillation with acetic acid.

this material with methane and propane resulted in two liquid layers. Additional careful distillation should concentrate this fraction to the point where it will crystallize, unless it contains small quantities of many of the possible hydrocarbons.

5. DISTILLATE BETWEEN 117° AND 124° C

Because the proportion of the material which distilled between 117° and 124° C was large, most of the effort was devoted to separating constituents in this range.

The refractive-index and volume curves, A_1 and A_2 of figure 1, show that the fraction distilling between 114° and 128° C contained originally a large quantity of paraffinic material which had a slight tendency to separate into two large volumes. An amount of *n*-octane [44] equivalent to about 1 percent of the crude petroleum was removed by crystallization from the distillate between 123° and 126° C.[11] Sub-

[11] R. T. Leslie and S. T. Schicktanz, BS J. Research 6, 377 (1931) RP282.

sequent distillations resolved the fraction into two more or less distinct ones boiling between 116° and 124° C and between 124° and 128° C. The lower-boiling fraction appeared to have the more complex composition. In previous publications there has been described in detail the isolation of a relatively large quantity of 2-methylheptane [12] [26] (about 0.5 percent of the petroleum) boiling at about 117° C, a smaller quantity of a mixture of naphthenes [13] (about 0.2 percent) boiling between 119.2° and 120.8° C, and of a small quantity of a naphthene (about 0.04 percent), boiling at about 123.4° C.[14]

The photomicrographs at the bottom of figure 1 show the crystal behavior of fractions from this range. The photograph of the material boiling at 116.9° C shows material identified as 2-methylheptane [26]. Those of the fraction at 119.8° C probably show 1,1-dimethylcyclohexane [34]. The three photographs of the same fraction were made successively and show two crystal forms.[15] At 120.2° C the crystals still resemble those at 119.8° C. At 120.3° C, however, the crystals resemble *m*-dimethylcyclohexane [16] [36]. The naphthenic material boiling at 123.4° C, thought to be *trans-o*-dimethylcyclohexane [39], differs in appearance from the crystals of the lower-boiling naphthenes. The fine crystals which appear in one of the photographs may be a small amount of *n*-octane. The result of adding more octane from the higher-boiling fractions is shown by the photograph of the "mixture."

The residue shown by curve B_2 between 116° and 122° C represents the relatively small quantity of material which concentrated after removing, by crystallization as completely as practicable, the constituents discussed above. The refractive-index curve B_1, figure 1, indicates that the material contained lower-boiling paraffinic constituents and higher-boiling naphthenes, which were probably an additional small quantity of the hydrocarbons mentioned above.

In addition to the 2-methylheptane [26], it is possible that this fraction also contained small quantities of 3-ethylhexane [29], 3,4-dimethylhexane [27], 3-methylheptane [28], 4-methylheptane [31], and 3-methyl-3-ethylpentane [32]. If they were present they would be found in the residue shown by curve B_2 of figure 1. Of the seven naphthenes which are reported to boil in this range [30, 33, 34, 35, 36, 39, and 40], three were found and tentatively identified [34, 35, 39]. Cycloheptane [30], because of its high freezing point, and *p*-dimethylcyclohexane [33], because of the absence of the characteristic crystals which it forms, appeared to be absent. 1-methyl-3-ethylcyclopentane [35] and isopropylcyclopentane [40] may be present in small quantities but were not detected.

6. DISTILLATE BETWEEN 125° AND 126° C

The approximately 7 liters of distillate obtained in the narrow range, 125° to 126° C, as shown by the volume curve B_2 of figure 1, was probably *n*-octane, as indicated by the minimum in the refractive-index curve B_1. The photomicrographs of crystals from these fractions show that the chief constituent behaves like *n*-octane [17] [44]. It is possible, however, that small quantities of 2,2,4,4-tetramethylpen-

[12] R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.
[13] R. T. Leslie, J. Research NBS **15**, 41 (1935) RP808.
[14] [15] R. T. Leslie, J. Research NBS **17**, 761 (1936) RP943.
[16] [17] R. T. Leslie and W. W. Heuer, J. Research NBS **18**, 639 (1937) RP1000.

tane [37], and 2,2,5-trimethylhexane [38], were also present since their boiling points are reported in this neighborhood. From the manner in which the refractive-index curve rises abruptly on either side of this narrow boiling range, it is apparent that the material also contained naphthenic constituents in small quantities, which were probably some of the *cis*-dimethylcyclohexanes [43, 46], 1-methyl-2-ethylcyclopentane [41], or isopropylcyclopentane [40]. The original 125° to 126° C distillate must have contained only a small percentage of naphthenic material, since the refractive-index of the large-volume fraction is very low and there are only small quantities of the fractions on either side which have high refractive indices.

7. DISTILLATE BETWEEN 127° AND 130° C

The material represented as "residue" in figure 1 was composed of "tailings" from several systematic fractionations and probably contained considerable cracked material. Treatment with silica gel, or other reagent for removing olefins, and distillation would return most of this material to lower-boiling fractions. Very little material actually distilled between 127° and 130° C. This might be expected since, as shown by figure 1, very few hydrocarbons are reported to boil in this range. If 2,3,5-trimethylhexane [45], *cis-o*-dimethylcyclohexane [46], and *n*-propylcyclopentane [47] were present, they must have been minor constituents. The next higher-boiling concentration of a constituent occurred at about 130° C, and the isolation of ethylcyclohexane from it has been reported by Rose and White.[18]

III. PROBABLE COMPOSITION OF A MIDCONTINENT PETROLEUM BOILING BETWEEN 100° AND 130° C

Most of the conclusions which have been reached in the investigation are summarized in table 2. This table presents, in addition to the relative quantities of constituents actually isolated, conclusions as to the probable presence or absence of each of the other hydrocarbons boiling between 98° and 131° C on which the author has found data in the literature. A column of the table also gives the approximate boiling ranges of the distillate from which constituents were isolated or in which constituents whose presence is uncertain might be expected to occur.

[18] F. W. Rose, Jr., and J. D. White, J. Research NBS 15, 151 (1935) RP817.

TABLE 2.—*Known hydrocarbons boiling between 100° and 130° C (approximately) with relation to the corresponding naphtha fraction of a midcontinent petroleum*

Compound	Reference number to table 1	Normal boiling point of pure compound	Approximate boiling range in which material occurred, if present	Relative volume found, referring to *n*-octane as unity [1]	Occurrence [2]
		°C	°C		
n-Heptane	1	98.4	95 to 100	1.1	*P*
2, 2, 4-Trimethylpentane	2	99.3			*A*
Methylcyclohexane	3	101.2	98 to 102	0.3[5]	*P*
Ethylcyclopentane	4	103.0 ±0.5	98 to 102		*S*
1, 1, 2-Trimethyl-2-ethylcyclopropane	5	103.5 to 104.5			*U*
1, 2-Dimethyl-1-ethylcyclopropane	6	104			*U*
2, 2, 3, 3-Tetramethylbutane	7	104 to 105.2			*U*
2, 2-Dimethylhexane	8	106 to 107	102 to 106		*S*
2, 5-Dimethylhexane	9	109.2 ±0.1	108.5 to 110.5		*S*
1-Methyl-1, 2-diethylcyclopropane	10	108 to 109			*U*
2, 4-Dimethylhexane	11	108 (750 mm)	108.5 to 110.5		*S*
1-Methyl-2-isobutylcyclopropane	12	109.5 to 110.5			*U*
Toluene	13	110.6[1]4	98 to 111	.3	*P*
2, 2, 3-Trimethylpentane	14	110.2	108.5 to 110.5		*S*
d-3, 5-Dimethylhexane	15	111 to 112	108.5 to 110.5		*S*
3, 3-Dimethylhexane	16	111 to 112	108.5 to 110.5		*S*
1, 2, 3-Trimethylcyclopentane	17	111.5 to 114	112 to 116		*S*
2, 3, 4-Trimethylpentane	18	112.8	108.5 to 110.5		*S*
1, 2, 4-Trimethycyclopentane	19	112.5 to 113	112 to 116		*S*
2, 3, 3-Trimethylpentane	20	113.6	112 to 116		*S*
2, 3-Dimethylhexane	21	113.9	112 to 116		*S*
2-Methyl-3-ethylpentane	22	114	112 to 116		*S*
1, 1, 2-Trimethylcyclopentane	23	113 to 114 (749 mm)	112 to 116		*S*
1, 1, 3-Trimethylcyclopentane	24	115 to 116	112 to 116		*S*
3, 3-Dimethylbicyclo-(0, 1, 3) hexane	25	115			*A*
2-Methylheptane	26	117.2	115 to 118	.2	*P*
3, 4-Dimethylhexane	27	118.7	116 to 122		*S*
3-Methylheptane	28	116.5 (746 mm)	116 to 122		*S*
3-Ethylhexane	29	118.8 to 119 (766 mm)	116 to 122		*S*
Cycloheptane	30	118 to 120			*A*
4-Methylheptane	31	118	116 to 122		*S*
3-Methyl-3-ethylpentane	32	118.5 to 119 (750 mm)	116 to 122		*S*
trans-1, 4-Dimethylcyclohexane	33	119.63	116 to 122		*S*
1, 1-Dimethylcyclohexane	34	119.8	116 to 122		*S*
1-Methyl-3-ethylcyclopentane	35	120.5 to 121 (756 mm)	116 to 122		*S*
trans-1, 3-Dimethylcyclohexane	36	120.40	118 to 122 [3]	.2	*P*
2, 2, 4, 4-Tetramethylpentane	37	122.30	120 to 126		*S*
2, 2, 5-Trimethylpentane	38	121 to 123	120 to 126		*S*
trans-1, 2-Dimethylcyclohexane	39	123.70	122 to 124	.04	*P*
Isopropylcyclopentane	40	123 to 124	122 to 126		*S*
1-Methyl-2-ethylcyclopentane	41	124	122 to 126		*S*
1, 1, 3, 3-Tetramethyl-2, 4-diethylcyclobutane	42	124 to 125			*U*
cis-1, 4-Dimethylcyclohexane	43	124.59	122 to 126		*S*
n-Octane	44	125.59	122 to 126	1.0	*P*
2, 3, 5-Trimethylhexane	45	129			*U*
cis-1, 2-Dimethylcyclohexane	46	130.04			*U*
n-Propylcyclopentane	47	130.6 ±0.2			*U*

[1] The numbers in this column give the estimated relative amounts by volume of the given hydrocarbons in the petroleum referred to normal octane as unity. To obtain the approximate magnitude of the percentage of hydrocarbon in the crude, these numbers should be multiplied by a factor which is roughly estimated, on the basis of the "over-all" losses, to lie between 1 and 1¾ (see abstract). Similarly, the approximate magnitude of the percentage in the 100° to 130° C fraction may be obtained by multiplying the numbers by a factor estimated to lie between 17 and 30. (Estimates in previous papers were made by doubling the actual quantities found in an attempt to compensate for losses. This factor is probably low.)

[2] Letters in this column have the following significance: *P*, present; *A*, presence in more than small amounts considered unlikely because of the properties of the compound; *S*, possibly present in amounts too small to be detected by the method used; *U*, presence considered unlikely because of structure or small quantity of distillate at its boiling point.

[3] This fraction also contained an unidentified naphthene boiling at about 119.8° C (possibly No. 34).

Of the distillate from the crude petroleum boiling between 100° and 130° C, *n*-octane [44] was by far the chief constituent. Reasonably careful distillation caused most of the *n*-octane to concentrate between 122° and 126° C. From this distillate a quantity of nearly pure hydrocarbon was isolated equal to about one-tenth of the volume with which the investigation was begun. Toluene [13] was the sole aromatic constituent and was present in a relatively large proportion. Distillation caused it to appear in a wide temperature range (98° to 111° C), and a quantity was isolated equal to about one-third the volume of *n*-octane. Methylcyclohexane [3] about equal in quantity to toluene was found in the distillate between 98° and 102° C. A quantity of 2-methylheptane [26] amounting to about one-fifth of the *n*-octane occurred in the material distilling between 115° and 118° C. At least three cycloparaffinic hydrocarbons were present in appreciable quantities in the distillate between the boiling range of the material containing the 2-methylheptane and that of the *n*-octane (*trans*-1,3-dimethylcyclohexane [36], *trans*-1,2-dimethylcyclohexane [39], and an unidentified hydrocarbon which may be 1,1-dimethylcyclohexane [34]). The other known hydrocarbons boiling in this range were in relatively small amounts, if at all. Between 126° and 130° C there was only a small quantity of distillate, indicating insignificant amounts of the few hydrocarbons whose boiling points are within the range. There was, however, distillate other than toluene between 102° and 115° C which though small, showed the presence of di- and trimethyl isomers of octane [8, 9, 11, 14, 15, 16, 18, 20, 21, 22] and possibly one or more of the cyclopentanes [4, 17, 19, 23, 24].

WASHINGTON, October 21, 1938.