

alcohols was done as follows: The water-soluble alcohols were extracted, and the fraction boiling below 100° C. was concentrated by preliminary distillation. The aqueous distillate was distilled fractionally in a special column with a rotating band. This column differed from that described under (b) on page 20 by the shape of the head, which was so constructed that azeotropic mixtures could be drawn off. Alcohols present in the reaction water were determined by a similar method. (Isobutyl alcohol and water form an azeotropic binary mixture boiling at 89.9° C.)

An ammoniacal silver solution was used as a test for aldehydes. Aldehydes were observed only when alcohols also were present in appreciable amounts. Ketones were represented by small amounts of acetone, which was precipitated as the phenylhydrazone by a saturated solution of p-nitrophenylhydrazine in 30 percent acetic acid. The precipitate was filtered with suction in a fritted-glass crucible, washed in a small amount of distilled water, and weighed after drying at 105° C.

In the single instance where phenols were obtained, they were shaken with sodium hydroxide, acidified with sulfuric acid, and extracted with ether.

DETERMINATION OF THE GASOLINE KNOCK RATING

Octane ratings were determined by the motor method with an I. G. testing motor.³⁵

INVESTIGATION OF LUBRICANT PROPERTIES OF THE HIGH-BOILING OIL FRACTIONS

In some instances the liquid reaction products contained small amounts of viscous oils. Lower-boiling components were removed by vacuum distillation, and the residual oils were examined at 20° and 50° C. in a Vogel-Ossag viscometer.

COMPOSITION OF LIQUID PRODUCTS FROM A LIFE TEST OVER $\text{ThO}_2\text{-Al}_2\text{O}_3$ CATALYST AT 300 ATMOSPHERES

DESCRIPTION OF DURABILITY EXPERIMENT

A life-test of a thoria-alumina (5:1 percent by weight of oxides) catalyst operated at 300 atmospheres and various temperatures was carried out. The catalyst was prepared by separate precipitation. The reactor contained 684 grams of catalyst in a layer 165 centimeters in length. The gas throughput corresponded to 205 liters of outlet gas per hour.

The experimental results are summarized in table 16 and figure 8. Operation was started at 425° C., measured by the aluminum block-

furnace surrounding the converter tube (allowing for the difference in heat removal, this temperature corresponds to 450° to 475° C. in the small-scale experiments reported in the earlier pages of this paper). In the first 13 days, catalytic activity was high; gaseous hydrocarbons were produced in relatively large amounts, but no dimethylether. All liquid reaction products were collected and subjected to precise fractionation for further study. A quantitative determination of the yields (grams per cubic meter of inert-free water gas) was made on the third day: 69 grams iso- C_4 -hydrocarbons, 20 grams C_3 +hydrocarbons, 17 grams C_3 + n - C_4 hydrocarbons, and 2.5 grams water-soluble alcohols.

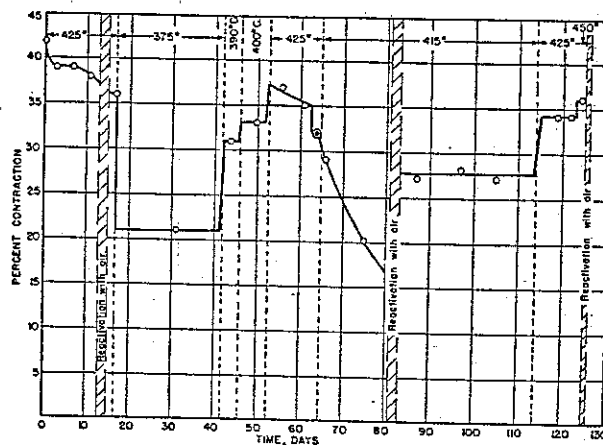


FIGURE 8.—COURSE OF A DURABILITY TEST (NO. 250) WITH $\text{ThO}_2+20\% \text{Al}_2\text{O}_3$ CATALYST AT 300 ATMOSPHERES.

On the fourteenth day, increased pressure drop across the catalyst bed indicated that reactivation treatment was necessary. Air was passed over the catalyst at a rate of 100 liters per hour for 24 hours at 425° C. (until carbon dioxide could no longer be detected in the air issuing from the converter). When treatment was completed, the pressure drop across the catalyst bed was again small. Operation was resumed at 425° C. Carbon monoxide conversion was approximately the same as before reactivation (70 percent), but the formation of low molecular-weight, gaseous hydrocarbons was small, and hydrogen conversion showed a corresponding drop from 65 to 60 percent.

On the evening of the seventeenth day, the temperature was decreased to 375° C. to obtain larger amounts of liquid hydrocarbons for a precise fractional distillation. It will be seen from the gas analyses made from the eighteenth to the forty-second day that conversion decreased with temperature. At 425° C., no dimethylether formed, whereas 3.8 percent by volume was obtained at 375° C.

³⁵ Jantsch, F., *Kraftstoff-Handbuch*: Frankh. Verlagsbuchhandlung, Stuttgart, 1940, p. 124.

one-hundred and twenty-second day is shown in table 16.

The gasol and liquid hydrocarbon fractions discussed below were collected at 425° C. during the first 13 days (experiment 250a) and at 375° C. in the period from the eighteenth to the forty-second day (250b). Figure 9 shows graphically the composition of the total reaction product obtained for these two periods.

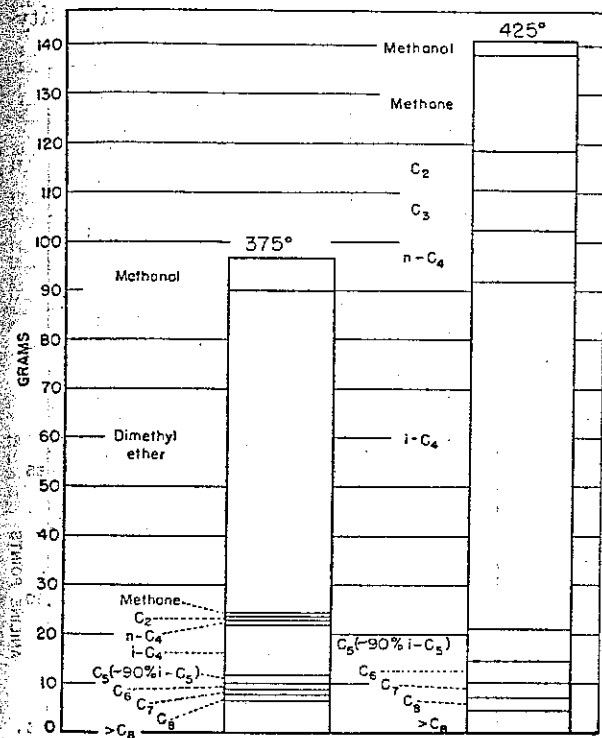


FIGURE 9.—COMPOSITION OF THE PRODUCT FROM EXPERIMENT 250 (ONE-STAGE TEST), GRAMS PER CUBIC METER (CO-H₂).

ANALYSIS OF THE GASOL FRACTION

The results of low-temperature distillations of the gasol fractions obtained during the two synthesis periods mentioned above are presented in table 17. The data are shown graphically in figure 10. The iso-butane yield in the first period (250a) was almost 15 times greater than that obtained in the second period (250b).

INVESTIGATION OF LIQUID HYDROCARBON FRACTION OBTAINED AT SYNTHESIS TEMPERATURE OF 425° C. (EXPERIMENT 250A)

The boiling point curve I (fig. 11) shows graphically the distillation analysis of the liquid reaction products obtained in experiment 250 at 300 atmospheres and 425° C. (fig. 8). Preliminary treatment consisted of washing the product with water, then lightly hydro-

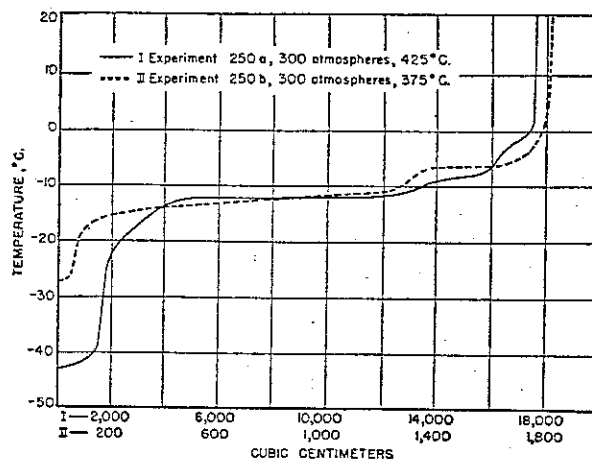


FIGURE 10.—DISTILLATION CURVES OF GASOL FRACTION FROM EXPERIMENT 250.

genating it in the presence of a nickel catalyst, and drying it over sodium. The physical constants for the distillation fractions are given in table 18.

The first plateau in the boiling-point curve, which includes fractions 1 to 8, consists almost entirely of 2-methylbutane and comprises about 35 percent of the total liquid hydrocarbons. The second plateau occurs at 60° C. (fractions 9 to 11). A number of hydrocarbons that may be considered as possible reaction products boil within this range: 2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane. The curve has one more plateau at 90° C. (fractions 14 to 17). A number of C₇ hydrocarbons distill between 78° and 100° C., as shown in table 18.

Figure 12; curve 1, shows the distillation curve for a quantity of 290 cubic centimeters of

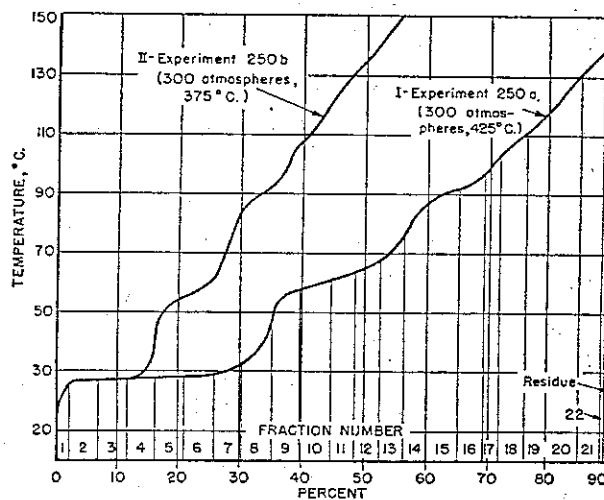


FIGURE 11.—DISTILLATION OF HYDROGENATED LIQUID HYDROCARBONS FROM EXPERIMENT 250.

TABLE 17.—Determination of gasol fractions from the isosynthesis

Samples	I	II
Experiment No.	250a	250b
Time of sampling during synthesis, days	3	31
Synthesis pressure, atmospheres	300	300
Synthesis temperature, °C.	425	375
Volume in-gas used, l.	633	517
Volume out-gas, l.	386	409
Distillation data, cc.:		
Forerunnings:		
CH ₄	14,100	420
C ₂ H ₄	400	170
C ₂ H ₆	2,380	70
Fraction, < -27° C.:		
C ₃ H ₆	355	0
C ₃ H ₈	1,435	0
Fraction, -27° to -7° C.:		
i-C ₄ H ₈ ^a	1,440	641
n-C ₄ H ₈ ^b	452	138
i-C ₄ H ₁₀	12,228	691
Fraction, -7° to +10° C.:		
i-C ₄ H ₈ ^a	173	263
n-C ₄ H ₈ ^b	265	22
n-C ₄ H ₁₀	1,262	65
Total volume, liters:		
Propene	(^c) 0.36	(^d) 0
Propane	1.43	0
i-butene	1.61	.90
i-butane	12.23	.69
n-butene	.72	.16
n-butane	1.26	.06
Yields, g./m ³ (CO+H ₂) feed gas:		
Methane	19.5	.7
Ethylene	1.0	.5
Ethane	6.2	.3
Propene	1.3	0
Propane	5.5	0
i-butene	7.8	5.2
i-butane	60.7	4.5
n-butene	3.5	1.0
n-butane	6.7	.3
C ₅ +hydrocarbons ^e	20.0	11.6
Alcohols	2.5	6.7
Dimethylether		65.7

^a With 64 percent H₂SO₄.

^b Hg(NO₃)₂ method.

^c Composition shown in next section.

^d Dimethylether removed from sample with concentrated NaCl and KOH.

^e Figure 9.

^f Figure 10.

* Contained 3.8 percent by volume dimethylether.

liquid hydrocarbons obtained later in the same experiment at the same temperature (425° C.). Distillation was carried out in a 1-meter band column. The refractive index was determined for each cubic centimeter of distillate collected (curve 2). For the higher fractions, aniline points also were determined (curve 3).

C₅ hydrocarbons.—It will be seen from figure 12 that iso-pentane represents 24 volume percent of the total reaction product (fraction 1) and n-pentane, 2.7 percent (fraction 2).

C₆ hydrocarbons.—There is no evidence of 2,2-dimethylbutane (b. p. 49.7° C., $n_D^{20}=1.36864$, $D_4^{20}=0.6494$). The presence of this hydrocarbon, which contains a quaternary carbon atom, can only be established by a large-scale precise fractional distillation of the 40° to 60°

C. fraction.³⁶ The following components were observed: 2,3-dimethylbutane (58.0° C., 24.6 cubic centimeters, 8.5 volume percent), 2-methylpentane (60.2° C., 17.9 cubic centimeters, 6.2 volume percent), and 3-methylpentane (63.2° C., 8.0 centimeters, 2.8 volume percent). The presence of methylcyclopentane (71.8° C., $n_D^{20}=1.4098$) is not evident from the distillation curve but is indicated on the refractive index curve, which shows a maximum of 1.3892 between 70° and 75° C. The quantity

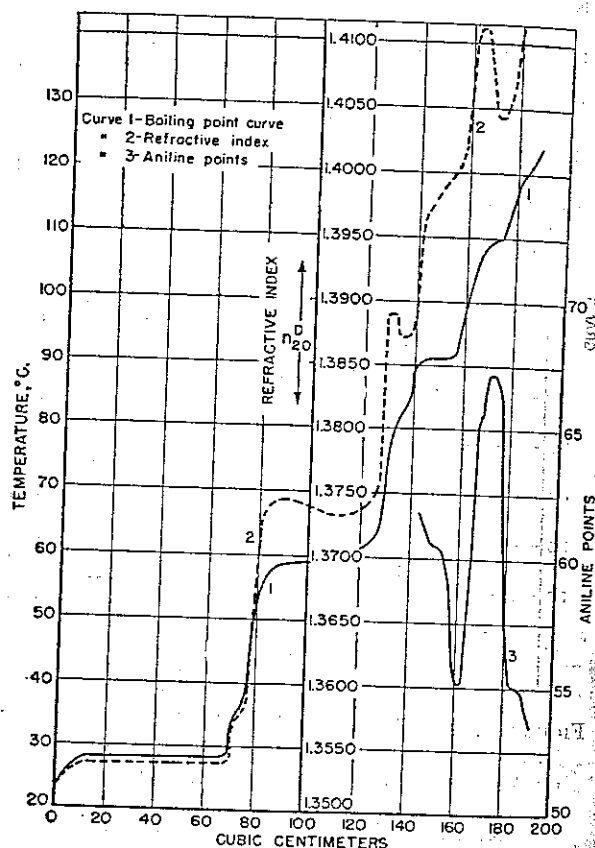


FIGURE 12.—ANALYSIS OF LIQUID HYDROCARBONS (290 CC.) FROM EXPERIMENT 250A (ThO₂+20% Al₂O₃ CATALYST, 300 ATMOSPHERES, 425° C.).

of methylcyclopentane represented about 0.7 percent (by volume) of the liquid hydrocarbon fraction. The appearance of methylcyclopentane is much more evident in the curve obtained from the precise distillation in a 1-meter band column of fractions 12, 13, and 14 of table 18. The data are summarized in figure 13 and table 19. A definite break occurs in the distillation curve in the region at which methylcyclopentane boils. The refractive index and density curves show well-defined maxima at 72° C. n-Hexane (b. p. 68.8° C., $n_D^{20}=1.37506$,

³⁶ Later found on systematic analysis by Pichler and Titzenthaler.

TABLE

Fraction No.

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TABLE 18.—Distillation analysis of the liquid hydrocarbon product (hydrogenated) from the isosynthesis (experiment 250a, 300 atmospheres, 425° C.)^a

Fraction No.	Boiling range, °C.	Physical constants			Size of fraction, percent by volume		Possible constituents					
		n _D ²⁰	D ₄ ²⁰	Specific dispersion	Individual	Total	Compound	Boiling range, °C.	n _D ²⁰	D ₄ ²⁰		
1	15.5-26.4					2.0						
2	26.4-26.9	1.3530	0.628	95.4		4.9						
3	26.9-27.0	1.3532	.628	95.4		4.7						
4	27.0-27.1	1.3532	.628	95.4		4.7						
5	27.1-28.0	1.3532	.624	95.4		4.7						
6	28.0-29.8	1.3538	.619	95.4		4.7	2MeC ₄ (iso-pentane)	27.95	1.355	0.61996		
7	29.8-31.8	1.3542	.625	98.2		4.7						
8	31.8-44.8	1.3575	.6305	98.3		4.7						
9	44.8-57.2	1.3712	.6580	96.8		4.8						
10	57.2-60.2	1.3738	.6598	96.9		4.9						
11	60.2-63.6	1.3739	.6597	97.0		3.8	2,3-di-MeC ₄	58				
12	63.6-67.2	1.3750	.6633	96.8		4.0	2-MeC ₅	60.2				
13	67.2-77.6	1.3818	.6778	96.1		3.8	3-MeC ₅	63.2				
14	77.6-86.3	1.3879	.6898	97.7		3.9	n-C ₆	68.8	1.37506	0.68942		
15	86.3-91.2	1.3948	.7076	96.8		4.9	Me-cyclo C ₆	71.8	1.4098			
16	91.2-95.3	1.4003	.7187	96.6		3.9	2,2-di-Me C ₅	78.9	1.3823	0.6737		
17	95-103.3	1.4074	.7323	101.2		2.7	2,4-di-Me C ₅	80.8	1.3824	.6726		
18							2,2,3-tri-Me C ₄	80.8	1.3894	.6901		
19							3,3-di-Me C ₅	86.0	1.3916	.6831		
20							2,3-di-Me C ₅	89.7	1.3920	.6944		
21							2-Me C ₆	89.7	1.3801	.6787		
22							3-Me C ₆	91.8	1.3887	.6900		
Residue	>140					10.6	1,1-di-Me-cyclo C ₅	87.5	1.4139	.7551		
							+1,2-di-Me-cyclo C ₅	91.8	1.4126	.7533		
							+1,3-di-Me-cyclo C ₅	91.5	1.4144	.7562		
							n-C ₇	98.4	1.3877	.68376		
							+Me-cyclo C ₆	100.6	1.4235	.7700		
							2,2,4-tri-Me C ₅	99.3	1.39157	.69194		
							hexa-Me C ₅	106.5				
							2,2-di-Me C ₆	107.0	1.3930	0.6936		
							+2,4-di-Me C ₆	109.0	1.39582	.6993		
							+2,5-di-Me C ₆	109.3	1.39295	.6945		
							2,2,3-tri-Me C ₅	110.3	1.4032	.7162		
							3,3-di-Me C ₅	111.0	1.3993	.7086		
							+2,3,4-tri-Me C ₅	113.4	1.4046	.7195		
							2-Me-3-Et-C ₅	114	1.4038	.7182		
							2,3,3-tri-Me C ₅	114.2	1.4075	.7258		
							+2,3-di-Me C ₆	115.7	1.40117	.71240		
							+2-Me C ₇	117.2	1.3947	.6978		
							+3,4-di-Me C ₆	117.8	1.4045	.7195		
							+4-Me C ₇	118.0	1.39814	.7163		
							3-Me-3-Et-C ₅	118.4	1.4081	.7256		
							3-Et-C ₆	118.9	1.4020	.7122		
							+3-Me-C ₇	119.0	1.3983	.7057		
							n-C ₈	125.6	1.39764	.70283		
							Et-cyclo C ₆	103.0				
							1-Me-1,2-di-Et-cyclo C ₅	108.9				
							1-Me-2-iso-C ₇ -cyclo C ₅	110-111				
							1,2,4-tri-Me-cyclo C ₅	113				
							Cyclo C ₇	117.5				
							+1,3-di-Me-cyclo C ₆	120				
							+1,4-di-Me-cyclo C ₆	123				
							1-Me-2-Et-cyclo C ₅	124				
							+1,2-di-Me-cyclo C ₆	126-129				
							C ₈ -cyclo C ₅	131.3				
							Et-cyclo C ₆	131.8				
							+1,3,5-tri-Me-cyclo C ₆	137-139				
							+1,2,4-tri-Me-cyclo C ₆	140-145				

^a See figure 11, curve 1.

D₄²⁰=0.65942) is present only in traces, if at all.³⁶

C₇ hydrocarbons.—The distillation curve in figure 12 flattens out between 80° and 84° C. and shows a break at 91° C. corresponding to a leveling off of the refractive-index curve. For the region between 90° and 100° C., the aniline points drop from 63 to 55.

The curves obtained by precise fractional distillation of fractions 12, 13, and 14 of table 18 (fig. 13 and table 19) and fractions 15, 16, and 17 of table 18 (fig. 14 and table 19) present a more accurate picture of the composition of the C₇ fraction. The presence of 2,2-dimethylpentane (b. p. 78.9° C.) (containing a quaternary carbon

atom) must be determined by precise fractionation of relatively large amounts of material. In any case, if hydrocarbons with quaternary carbon atoms are present among the low-boiling compounds, there are only small amounts. (In subsequent analyses, Fichler and Titzenthaler were able to establish the presence of 3,3-dimethylpentane.)

The values for the refractive index and the density indicate that, of the two hydrocarbons boiling at 80.8° C., 2,4-dimethylpentane and 2,2,3-trimethylbutane, only the former is present. It represents 2.7 percent of the liquid products.

There is no evidence of the presence of

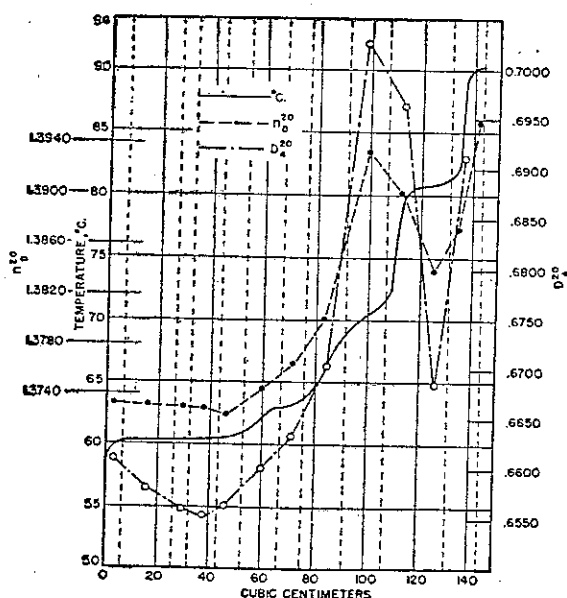


FIGURE 13.—PRECISE DISTILLATION OF FRACTIONS 12, 13, AND 14 (144 CUBIC CENTIMETERS) OF EXPERIMENT 250A.

3,3-dimethylpentane (b.p. 86.0° C.), 2,3-Dimethylpentane 89.7° C.), 2-methylhexane (89.7° C.), 3-methylhexane (91.8° C.), and the dimethylcyclopentanes (87.5°, 91.5°, and 91.8° C.) make up 8 percent of the distillation product in figure 12 and 10 percent of that in figure 14. The dimethylcyclopentane content calculated from the aniline points is 2.5 and 3.9 percent, respectively, of the total liquid hydrocarbons. No n-heptane (98.4° C.) was detected, and it probably occurs only in traces, if at all. Methylcyclohexane (100.8° C.) probably represents about 2 volume percent of the total liquid hydrocarbons. The aniline point for fraction 9 of figure 14 (100° to 106° C.) indicates a naphthene content of 81 percent. This high naphthene content corresponds to a well-defined maximum in the refractive index curve of figure 12. No such maximum appears in figure 14, where the refractive indexes were determined simultaneously for larger fractions, whereas in the distillation represented in figure 12 the index was determined for each cubic centimeter collected.

In general, the naphthene content increases with the boiling points of the isosynthesis reaction products, ranging from nothing for the lower fractions in figure 13 to 81 percent for fraction 9 in figure 14. In all, 19 cubic centimeters of naphthenes were obtained from 144 cubic centimeters of hydrocarbon distillate analyzed in figure 13 and 67 cubic centimeters from 145 cubic centimeters of distillate in figure 14.

At about 110° C., the refractive index curve again shows a minimum and the aniline point curve a maximum. At this temperature, aliphatic C₈ hydrocarbons distill over. Reasoning by analogy with the low-boiling hydrocarbons, it is probable that the principal compounds are 2,4-dimethylhexane (109° C.) and 2,5-dimethylhexane (109.3° C.). Under certain conditions, probably 2,2,3-trimethylpentane (110.3° C.) and possibly 2,2-dimethylhexane (107° C.) and 3,3-dimethylhexane (111° C.) occur.

It will be seen from curve I of figure 11 that there are no plateaus corresponding to the boiling points of fractions 18 to 22. These were subjected to a second distillation in the band column and separated into 12 subfractions whose physical constants were determined. The results of this distillation are summarized in table 19. The naphthene content is again high, reaching a value of 100 percent between 104° and 106° C. As noted above, between 108° and 114° C. it drops to 30 to 33 percent but rises above 50 percent from 117° to 127° C., reaching 100 percent again at 134° C. The octane fractions distill in the middle temperature region, where the amount of paraffin hydrocarbons may be as high as 70 percent. Individual octanes could not be isolated by the distillation procedure used. Table 18 contains the physical constants for the C₈ hydrocarbons. Those whose existence appears most probable by analogy with the lower fractions are indicated by a cross.

Calculations showed that of the 203.9 cubic centimeters of hydrogenated liquid hydro-

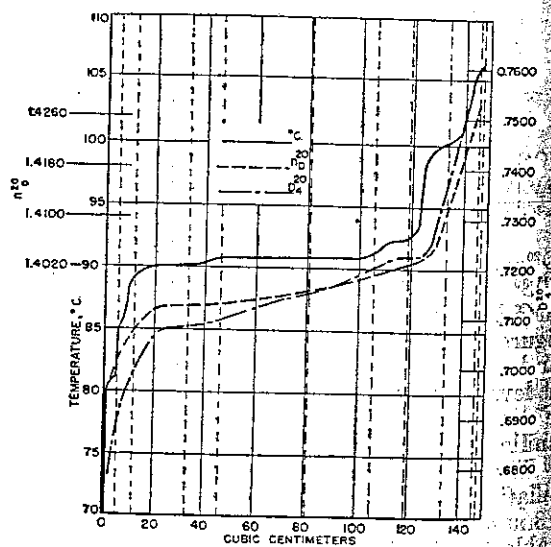


FIGURE 14.—PRECISE DISTILLATION OF FRACTIONS 15, 16, AND 17 (145 CUBIC CENTIMETERS) OF EXPERIMENT 250A.

TABLE 19.—Precise distillation of selected fractions of liquid hydrocarbon product (experiment 250a, 300 atmospheres, 425° C.)

A.—Fractions 12, 13, and 14, table 18 (fig. 13)

Fraction No.	Boiling range, °C.	Physical constants			Volume, cc.	Volume, percent naphthene	Volume, naphthene, cc.
		n _D ²⁰	D ₄ ²⁰	Aniline point, °C.			
1	57.2-60.3	1.3734	0.6610	-----	6.2	-----	-----
2	60.3-60.4	1.3731	.6580	-----	20.2	-----	-----
3	60.4-60.4	1.3730	.6558	-----	60.2	-----	-----
4	60.4-60.5	1.3728	.6552	-----	10.9	-----	-----
5	60.5-61.0	1.3724	.6563	-----	9.3	-----	-----
6	61.0-63.0	1.3745	.6598	-----	14.2	-----	-----
7	63.0-63.6	1.3762	.6631	-----	9.0	-----	-----
8	63.6-69.0	1.3800	.6704	63.5	15.5	20	19
9	69.0-71.8	1.3933	.7023	48.9	15.5	56	
10	71.8-80.8	1.3900	.6960	64.0	12.2	33	
11	80.8-81.4	1.3838	.6685	75.1	12.8	8	
12	81.4-90.3	1.3891	.6910	69.2	8.0	20	
13	90.3-90.4	1.3958	-----	62.2	4.0	40	

B.—Fractions 15, 16, and 17, table 18 (fig. 14)

1	49.9-80.9	1.3831	0.6774	-----	4.7	-----	67
2	80.9-89.2	1.3901	.6944	67.7	7.0	8	
3	89.2-90.4	1.3959	.7074	61.9	22.0	33	
4	90.4-90.9	1.3963	.7087	61.1	13.1	38	
5	90.9-91.0	1.3972	.7129	59.8	33.4	42	
6	91.0-91.4	1.3997	.7171	57.4	25.8	54	
7	91.4-92.3	1.4018	.7223	55.8	12.8	58	
8	92.3-100.1	1.4039	.7228	55.1	14.4	62	
9	100.1-106.3	1.4187	.7493	42.6	12.0	81	
10	106.3-106.4	1.4290	.7617	-----	1.8	-----	

C.—Fractions 18, 19, 20, and 21, table 18

1	88.8-98.2	1.4011	0.7191	57.9	6.0	57	3.4
2	98.2-104.6	1.4165	.7461	46.7	18.0	93	16.7
3	104.6-106.3	1.4219	.7544	43.6	8.4	100	8.4
4	106.3-108.0	1.4180	.7496	49.2	9.6	87	8.4
5	108.0-108.3	1.4122	.7396	57.4	18.0	60	10.8
6	108.3-110.2	1.4054	.7257	65.6	10.0	30	3.0
7	110.2-113.8	1.4069	.7317	64.7	14.0	33	4.6
8	113.8-117.6	1.4127	.7443	61.4	8.4	47	3.9
9	117.6-127.4	1.4202	.7592	59.8	38.7	50	19.3
10	127.4-134.1	1.4327	.7733	46.0	35.0	97	34.0
11	134.1-136.5	1.4412	.7866	33.9	24.0	100	24.0
12	136.5-141.0	1.4461	.7983	32.5	13.8	100	13.8

carbons distilled (fractions 18 to 22), 150.3 cubic centimeters consisted of naphthenes.

In table 20 is summarized the information discussed in the preceding pages. The composition of the total hydrogenated liquid hydrocarbon product from experiment 250a is shown, as well as the distribution of the paraffin hydrocarbons in the -100° C. fraction. The definite break at 100° C. in the precise distillation data of table 19B at fraction 8 (62 percent naphthene) and fraction 9 (81 percent naphthene) and 19C at fraction 2 (93 percent naphthene) indicates the presence of small

amounts of paraffin hydrocarbons (possibly 2,2,4-trimethylpentane) together with methylcyclohexane.

Only paraffins and naphthenes were obtained from the distillations discussed above, because the product had been hydrogenated before distillation. The olefin and aromatic content of the crude products was determined by separate distillation in a glass spiral column of the unhydrogenated liquid product. No attempt was made to isolate individual hydrocarbons. Table 21 contains the results obtained in this way. The average olefin content based on the