TABLE 20.—*Probable composition of the liquid hydrocarbon product (hydrogenated) from the isosynthesis (experiment 250a, 300 atmospheres, 425° C.).*

Constituent	Total percent	Percent of −100° C. paraffin hydrocarbons
C_5 paraffins	34	
2-Me-C_4		90
n-C_5		10
C_6 paraffins[a]	21	
2-Me-C_5		35
3-Me-C_5		16
2,3-Di-Me-C_4		49
n-C_6		[b]
C_7 paraffins[c]	10	
2, 4-Di-Me-C_5		[d] 35
2-Me-C_6		[d] 65
3-Me-C_6		
2,3-Di-Me-C_5		
C_8 paraffins	5	
Naphthenes	19	
C_8[e]	11	

[a] Cyclohexane was not found.
[b] In subsequent experiments, 0.6–3.4 percent 2,2-dimethylbutane and 3–8 percent n-hexane were obtained under various conditions.
[c] 2,2-dimethylpentane, 3,3-dimethylpentane, 3-ethylpentane, 2,2,3-trimethylbutane, and n-heptane were not found.
[d] Approximate values.
[e] Not determined.

values in table 21 is 39.3 percent. The olefin content for the entire product calculated for an average carbon number is 34 percent. No aromatic compounds were found in the first three fractions (table 21). Beginning with fraction 4, the aromatic content increased with the boiling point of the fraction.

TABLE 21.—*Determination of the olefin and aromatic content of the liquid product obtained in the isosynthesis (experiment 250a, 300 atmospheres, 425° C.).*

Boiling range, °C.	Volume percent	Average C-No.	Iodine-thiocyanate number	Olefins, weight percent	Aromatics, percent
21–65	46.0	5.33	124.8	39.1	0
65–95	15.2	6.87	65.5	24.9	0
95–125	10.9	7.72	73.4	31.2	0
125–150	10.9	8.89	102.4	50.3	5
150–175	5.4	~9.9	100.4	55.0	3
175–195	5.0	~11	102.5	62.3	31

ANALYSIS OF LIQUID HYDROCARBON PRODUCTS OBTAINED AT SYNTHESIS TEMPERATURE OF 375° C. (EXPERIMENT 250B)

Curve II of figure 11 shows the distillation analysis of the product obtained in experiment 250 at 375° C. This product was subjected to the same preliminary hydrogenation treatment as that whose distillation analysis is shown in curve I. However, owing to a particularly high olefin content, complete saturation was not obtained in a single hydrogenation. This is apparent from the boiling-point curve and from the physical constants for the individual fractions. The curve was drawn to show the increase in high-boiling hydrocarbons at low temperatures. Products formed at 425° C. contained approximately 11 percent of hydrocarbons boiling above 140° C., whereas those formed at 375° C. contained about 48 percent. The general character of curves I and II is similar. The total olefin content is higher (76 percent, table 22) than for the product obtained at 425° C. in experiment 250a (25 to 39 percent, table 21).

TABLE 22.—*Olefin and aromatic contents of the liquid products from experiment 250b (ThO_2-Al_2O_3, 300 atmospheres, 375° C.).*

Boiling range of fraction, °C.	Olefins, weight percent	Aromatics, weight percent
65–95	51.3	0
95–125	88.8	0
125–150	91.2	0
Total	76	

It is interesting to note that in isosynthesis the olefin content of the reaction products increases as the synthesis temperature decreases and the boiling range of the products increases, whereas in the normal hydrocarbon synthesis at atmospheric and medium pressures the olefin content decreases under the same conditions. No aromatics were present in the compounds boiling between 65° and 150° C.

The higher-boiling fractions of the hydrogenated product obtained at 375° C. were vacuum-distilled. Table 23A shows the results of this distillation calculated to standard conditions.

The 150° to 200° C. fraction had a strong terpene odor and produced a violent reaction in the presence of bromine, which was accompanied by the evolution of white hydrobromic vapors. Appreciable amounts of hexamethylbenzene distilled with the 200° to 275° C. fraction. Recrystallization produced 6 grams of the pure compound identified by its melting point and a mixed melting point. The residue was a reddish-brown oil that showed green fluorescence and whose viscosity was 141 centipoises at 20° C. and 21 centipoises at 50° C. (Vogel-Ossag viscosimeter). Treatment three times with Fuller's earth made the color of the oil considerably lighter; its viscosity dropped to 93 centipoises at 20° C. and 15 centipoises

TABLE 23.—*Distillation of liquid hydrocarbon products (hydrogenated) obtained in the isosynthesis under various conditions*

A.—Experiment 250b, 300 atmospheres, 375° C., ThO_2–Al_2O_3

Fraction No.	Boiling range, °C.	Volume, percent	n_D^{20}	D_4^{20}	Aniline point, °C.	Specific dispersion
1	150	56. 1				
2[a]	150–200	15. 4	0. 819	1. 4585		
3	200–275	10. 1	. 885	1. 4952		
4	275–310	3. 3	. 905	1. 5143		
5[b,c]	>310	9. 3	. 948			

B.—150 atmospheres, 375° C., ThO_2

0[d]	25. 0– 27. 4					
1	27. 4– 37. 7		1. 3641	0. 6520		115. 6
2	37. 7– 59. 3		1. 3752	. 6558		106. 0
3	59. 3– 60. 5		1. 3730	. 6539		95. 3
4	60. 5– 60. 7		1. 3729	. 6535		95. 3
5	60. 7– 62. 1		1. 3730	. 6548		97. 3
6	62. 1– 76. 7		1. 3851	. 6746	55. 4	106. 9
7	76. 7– 80. 2		1. 3893	. 6819	61. 7	104. 6
8	80. 2– 81. 1		1. 3849	. 6733	72. 1	96. 8
9	81. 2– 81. 3		1. 3849	. 6734	72. 9	98. 9
10	81. 3– 82. 0		1. 3859	. 6738	71. 2	98. 8
11	82. 0– 85. 4		1. 3900	. 6790	64. 5	107. 2
12	85–4– 89. 8		1. 3962	. 6993	58. 4	105. 4
13	89. 8– 90. 9		1. 3981	. 7119	59. 0	101. 8
14	90. 9– 91. 4		1. 3992	. 7161	57. 9	97. 6
15	91. 4– 97. 3		1. 4032	. 7237	52. 4	95. 6
16	97. 3–108. 6		1. 4096	. 7345	52. 4	98. 8
17	108. 6–109. 8		1. 4046	. 7248	63. 7	99. 5
18	109. 8–109. 9		1. 4040	. 7232	65. 0	99. 6
19	109. 9–114. 6		1. 4067	. 7283	62. 0	97. 6
20	114. 6–117. 7		1. 4147	. 7446	53. 5	99. 0
21	117. 7–120. 0		1. 4182	. 7530	51. 1	96. 8
22	120. 0–128. 0		1. 4216	. 7617	49. 8	96. 6
23	145. 4–154. 4		1. 4290	. 7710	55. 2	102. 2
24	154. 4–161. 9		1. 4320	. 7758	52. 5	105. 7
25	161. 9–191. 4		1. 4403	. 7906	51. 1	108. 9
26[e]	191. 4–225. 0		1. 4620	. 8269	39. 6	120. 0
27[f]	>225. 0					

C.—30 atmospheres, 475° C., ThO_2

1	25. 0– 59. 9	2. 1	1. 3690			
2	59. 9– 60. 3	2. 1	1. 3736			
3	60. 3– 63. 5	2. 1	1. 3740			
4	63. 5– 68. 6	2. 1	1. 3852			
5	68. 6– 70. 5	2. 1	1. 3948			
6	70. 5– 78. 5	2. 1	1. 4004			
7	78. 5– 87. 5	2. 1	1. 3942			
8	87. 5– 90. 2	2. 1	1. 4019			
9	90. 2– 90. 3	2. 1	1. 4030			
10	90. 3– 91. 0	2. 1	1. 4049			
11	91. 0– 91. 5	2. 1	1. 4078			
12	91. 5– 94. 0	2. 1	1. 4101			
13	94. 0– 98. 5	2. 1	1. 4108			
14	98. 5–104. 5	2. 1				
15	104. 5–106. 0	2. 1				
16	106. 0–108. 0	2. 1				
17	108. 0–110. 0	2. 1				
18[g]	110. 0–161. 6	41. 3				
19[h]	>161. 6	23. 0				

[a] Terpene odor.
[b] Fluorescent oil.
[c] Loss, 5.8 percent.
[d] This fraction is included in the gasol hydrocarbons.
[e] Total volume in 25°–225° C. range=443 cc.
[f] This fraction was 10 cc. in volume.
[g] Total volume in 25°–161.6° C. fraction=369 cc.
[h] This fraction was 116 cc. in volume.

at 50° C. The crude oil solidified at −14° C., the purified product at −26° C.

COMPOSITION OF LIQUID PRODUCTS OBTAINED UNDER VARIOUS SYNTHESIS CONDITIONS

THORIUM OXIDE CATALYST, 150 ATMOSPHERES, 375° C.

Distillation curve I, figure 15, corresponds to the liquid reaction product from an experiment with an unpromoted thorium oxide catalyst at 375° C. and 150 atmospheres. The hydrogenated hydrocarbon mixture was washed with water, dried over sodium, and distilled in a 1-meter band column. The product was separated into 27 fractions (table 23B).

Curve I, figure 15, may be compared with curve II of figure 11, which was derived for a product obtained at the same temperature (375° C.). It will be seen that the molecular size of the hydrocarbons depends not only on the synthesis temperature and pressure but on the activity of the catalyst. 2-Methylbutane again occurs in the C_5 fraction, but in this experiment it was only partly recovered. The characteristic break at 60° C. (2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane) again appeared in the C_6 fraction. A plateau in the C_7 portion of the curve appeared at 80° C. (probably 2,4-dimethylpentane). 2- and 3-Methylhexane as well as 2,3-dimethylpentane and the naphthenes 1, 2- and 1,3-dimethylcyclopentane distilled at 90° C. The portion of the curve corresponding to the C_8 fraction showed a definite plateau at 110° C. (2,4- and 2,5-dimethylhexane).

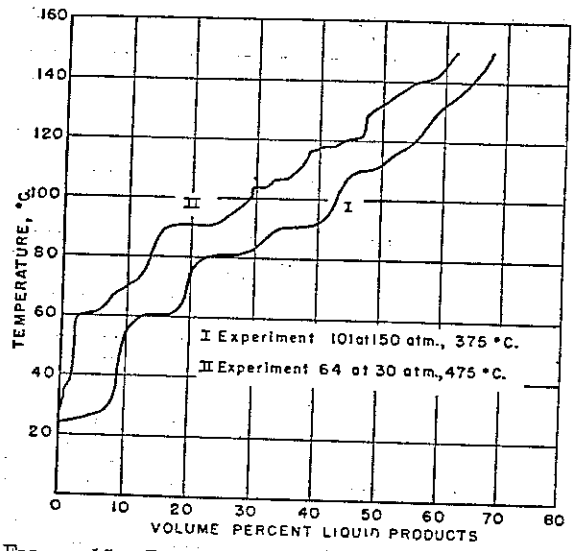

FIGURE 15.—DISTILLATION OF HYDROGENATED LIQUID HYDROCARBONS OBTAINED UNDER SPECIAL ISOSYNTHESIS CONDITIONS.

The product contained only small amounts of normal paraffins. The naphthene content increased with the boiling point of the products. However, it will be seen from the aniline points that naphthene formation was lower than for the product synthesized at higher temperatures.

THORIUM OXIDE CATALYST, 30 ATMOSPHERES, 475° C.

The last example is a distillation curve (curve II, fig. 15, and table 23C) obtained from a product synthesized at a pressure known to give poor yields (30 atmospheres). To attain comparable yields, a high synthesis temperature of 475° C. was necessary.

Comparison of the distillation for the product prepared at 30 atmospheres (curve II, fig. 15) with curve I shows that n-pentane (36.2° C.) and probably n-hexane (69.0° C.) occur in small amounts. 2-Methylbutane was produced but was not recovered with the liquid hydrocarbons. No break occurred in the C_7 region at 80° C. (2,4-dimethylpentane), but a hydrocarbon mixture distilling at 90° C. was obtained.

Curve I of figure 15 and the previous curves showed a well-defined break at 110° C. corresponding to the C_8 fraction, whose presence was indicated by a drop in the aniline point. No such plateau was observed in the curve for the product obtained at 30 atmospheres. On the other hand, the curve showed a number of small breaks above and below 110° C., which probably indicate the presence of naphthenes.

The fact that the refractive indexes are consistently higher in curve II indicates that the naphthene content of the hydrocarbons increases with the synthesis temperature.

COMPOSITION OF ALCOHOL FRACTION

In general, it is reported that the determination of the alcohol content of reaction products is by acetylation. Active thorium oxide-aluminum oxide catalysts produced only small amounts of alcohol. After the liquid reaction product was washed with water, it was dried over sodium. No reaction with sodium was observed, indicating that little or no alcohol was present.

The reaction water contains alcohols in amounts that vary according to the operating conditions. These alcohols are concentrated by preliminary distillation in the range boiling below 100° C. and then subjected to precise fractional distillation in a rotating band column.

The boiling points for methanol and for azetropic mixtures containing lower-boiling alcohols and water are listed in table 24.

TABLE 24.—*Boiling points of azeotropic mixtures containing lower-boiling alcohols and water*

Alcohols	Weight percent H_2O	Boiling point, °C
Methyl	0	64.7
Ethyl	4.43	78.1
n-propyl	28	87.7
Isopropyl	12.3	80.4
n-butyl	37.8	92.6
Isobutyl	33.2	89.8
Secondary butyl	27.3	87.5
Amyl	54.4	95.8
Isoamyl	50.5	94.7

Curves I and II, figure 16, show the distillation curves for the alcohols from experiment 250a (425° C.) and 250b (375° C.), respectively. Methanol was the only alcohol present in the aqueous reaction product.

Figure 17 shows the distillation curve of the alcohols from experiment 159 (thorium oxide catalyst, 150 atmospheres, 370° C.). In this experiment, both methanol and isobutyl alcohol were obtained. Repeated distillation of the latter compound resulted in an aqueous and an alcohol layer, from which pure isobutyl alcohol was recovered and identified by its boiling point (108° C.), density (D_4^{20}=0.8029), and refractive index (n_D^{20}=1.39583).

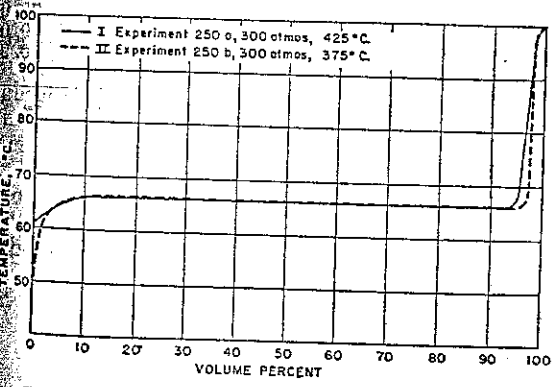

FIGURE 16.—DISTILLATION CURVE OF WATER-SOLUBLE —100° C. FRACTION FROM EXPERIMENT 250.

ANTI-KNOCK RATING OF THE HYDROCARBONS

Table 25 lists the motor octane ratings of the liquid hydrocarbons synthesized in experiment 250a, together with their boiling points and the percent of the total product which they represent. Iso-pentane (2-methylbutane) and 2,3-dimethylbutane are the predominating compounds.

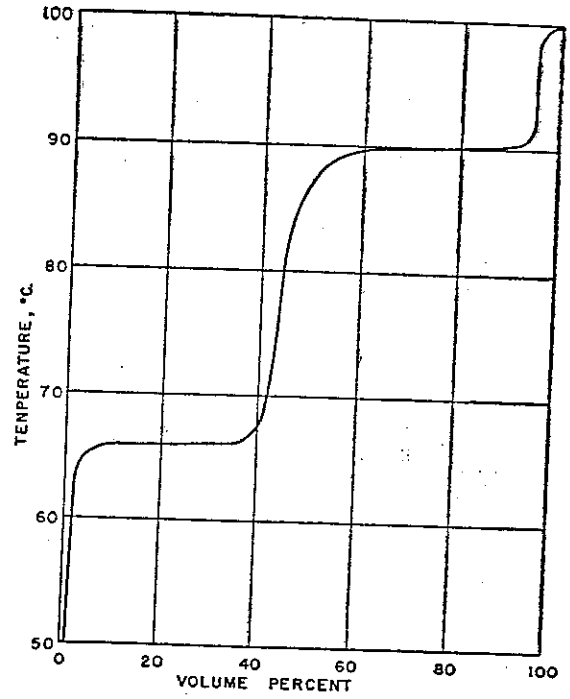

FIGURE 17.—DISTILLATION CURVE OF WATER-SOLUBLE, —100° C. FRACTION FROM EXPERIMENT 159 (150 ATMOS., 370° C.).

It is known that the mixed octane rating of a gasoline does not coincide with the average octane number calculated for a mixture of hydrocarbons according to the law of mixtures. The experimental value may be higher or lower, depending on the hydrocarbon. If, nevertheless, the average octane rating is determined according to the law of mixtures for the hydrocarbons listed in table 25, calculations show that hydrocarbons boiling below 140° C. (89 percent of the liquid reaction product) have an average octane rating of 80 to 81; those boiling below 100° C. (70.4 percent) have an average rating of

TABLE 25.—*Octane ratings for isosynthesis hydrocarbons (experiment 250a)*

C-No.	Hydrocarbon	Boiling point, °C.	Percent of liquid hydrocarbons	Motor octane number
5	2-methylbutane	27.9	31	89
5	n-pentane	36.1	3	64
6	2-methylpentane	60.2	7	73
6	3-methylpentane	63.2	3	75
6	2, 3-dimethylbutane	58.0	11	95
6	methylcyclopentane	71.8	1.4	82
7	2-methylhexane	89.7	~2	45
7	3-methylhexane	91.8	~2	(65)
7	2, 3-dimethylpentane	89.7	~2	89
7	2, 4-dimethylpentane	80.8	4	82
7	{1, 2- and 1, 3-dimethylcyclopentane	91.8 91.5 }	4	(80)
7	methylcyclohexane	100.8	1.5	71
8	octane mixture	>99	4	
8	naphthene		13	} (~70)

84, and those boiling below 80° C. (56.4 percent) have an average rating of 86. Determination of the octane rating for the fraction of unhydrogenated product from experiment 250a distilling below 150° C. with an I. G. testing motor gave a value of 77.4. The octane rating was the same when the gasoline fraction boiling from 150° to 180° C. was included. Addition of 0.08 percent tetraethyl lead raised the octane rating to 89.9.

The octane rating for the hydrogenated product from experiment 250b (thorium oxide-aluminum oxide, 300 atmospheres, 375° C.) was also 77.3 (table 26). Compounds 5 to 8 in table 26 were obtained from experiments at 30 and 150 atmospheres. Here, too, the octane rating for the unhydrogenated hydrocarbons boiling below 150° C. was 78 to 80.5.

Since iso-C_4 hydrocarbons are the principal product of the synthesis when the reaction products are used as high-capacity fuels, it should be possible to subject iso-butane, iso-butene, and n-hydrocarbons to a common alkylation process. Addition of tetraethyl lead to the gasoline obtained by alkylation gives octain ratings of 100 or more and can be combined with the primary gasoline prepared by isosynthesis. According to experiment 250a, in which approximately 60 grams of iso-C_4 hydrocarbons were obtained for every 20 grams of liquid hydrocarbons, the mixture should consist of 6 parts of alkylation gasoline and 1 part of isogasoline boiling below 180° C. Addition of 0.08 volume percent of tetraethyl lead to a mixture of this type yields a motor octane rating of 99.2.

TABLE 26.—*Octane ratings for various gasolines prepared*

No.	Experiment number	Catalyst	Pressure atmosphere	Temperature, °C.	Boiling range, °C.	Washed with 30 percent $CaCl_2$ solution	Hydrogenated	$Pb(C_2H_5)_4$ added percent	Reid vapor pressure	Octane number
1	250a	ThO_2 Al_2O_2	300	425	<150	—	—	—	0.64	77.4
2	250a	do	300	425	<180	—	—	—	.71	77.4
3	250a	do	300	425	<180	—	—	0.08	.71	88.9
4	250b	do	300	375	<180	—	+	—	.46	77.3
5	64	ThO_2	30	500	<150	+	—	—	.70	79.5
6	101a	do	150	450	<150	+	—	—	.54	78.0
7	101b	do	150	375	<150	+	—	—	.75	79.0
8	159	do	150	370	<150	+	—	—	.71	80.9