Report

The Progress of the Research Commission on "Continued Development of the Gasoline Synthesis from CO and H_2, Especially in the Direction of a Direct Synthesis of Isoparaffins. (SS6132-9798/42)."

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Translated by W. Oppenheimer

On the Direct Synthesis of Isoparaffins from CO and H_2.

During experimental work on the behavior of various oxides as catalysts for the conversion of CO and H_2 to hydrocarbons and oxygen-containing organic compounds, it was discovered that catalysts based on thorium are outstandingly well suited for the synthesis of branched hydrocarbons.

The process requires an operation with increased pressures, and the optimal range of pressure is determined by the nature of the catalyst. As one-component catalysts, the thorium catalysts occupy a special position, because with their assistance and with relatively low pressure, for example, 30 atmospheres, branched hydrocarbons have been obtained in large quantities. This paper deals only with these thorium catalysts because only the work done in this field

General.

Water gas with a $CO:H_2$ ratio of 1:1 to 1.2:1 was used generally as the starting gas of the synthesis. Such a gas mixture corresponded to the consumption of both components, under optimal conditions of the synthesis.

A series of experiments have been carried out in which dimethylether and H_2 have been used as starting substances. These experiments, which have been carried through chiefly for the clarification of the reaction mechanism, are not included in this report.

The synthesis has been carried out in CO-proof pressure pipes, that is, partly in copper-lined unalloyed steel pipes and in another part in unlined alloyed steel pipes, for example V_2A or Sicromal (a silica, chromium, aluminum alloy) steel.

The inner width of the reaction pipes was generally 15 mm.; however, pipes with an inner width of 25 mm. could also be used without any noticeable harm to the conversion.

The throughput of gas has been determined by measuring the expanded final gases and by the contraction calculated from the nitrogen values. We operated, generally, with a final gas quantity of 10 liters per hour per 28 grams thorium catalyst, (based on experiments on the influence of the flow rate). With a contraction of 50 percent, this corresponds to 20 liters per hour per 28 grams thorium catalyst. Under these conditions, the yield per space and time is about 10 times larger than under normal con-

The composition of the gasol hydrocarbons in the resulting
reaction products which are removed from the final gas by cooling or
by active carbon has always been determined by low temperature dis-
tillation, and the liquid hydrocarbons (mostly the hydrogenized pro-
ducts) have been determined by fine distillation. From each fraction
of the liquid hydrocarbons, the refractive index, density,
iodine-thiocyeno number, aniline-point, etc. have been determined.
Moreover, the resulting gasoline products, after the proper distilla-
tion and the standardizing of the vapor pressure in the crude and
the refined state with and without the addition of lead tetraethyl,
have been tested in an I.G. testing motor, according to the motor
method, for their resistance to knocking.

The Thorium Catalyst.

The best thorium catalysts are produced by precipitation
of thorium salt solutions, generally by precipitation of the basic
carbonate by sodium carbonate from the nitrate solutions. The
freshly precipitated contact was washed until it was free of alkali,
because small amounts of alkali reduce the activity of the thorium
catalyst and require a higher reaction temperature. After the wash-
ing, the contact was dried first at 110°C., then it was granulated,
and finally it was sintered in an air current at 300° to 400°C.

The lifetime of the thorium catalyst was very long under
the conditions of the iso-synthesis. Catalysts which, after a long
operation, exhibited an inner resistance due to the formation of
carbon could be regenerated by treating them with air at the con-

The Reaction Products as Dependent
on the Conditions of the Synthesis.

The kind of the resulting reaction products is dependent on the following conditions: The composition and the method of production of the catalyst, the temperature, the pressure, the time during which the gas stays in the contact space, the operation (CO and H_2) in several stages, the material of the reaction pipes, etc. Figure 1 shows the composition of the reaction products as dependent on the synthesis temperature with a pressure of 150 atmospheres and a flow rate of the gases corresponding to 10 liters final gas per hour per 28 grams of catalyst.

The quantity of the resulting alcohols and of other oxygen-containing organic compounds, which prevail at lower temperature, especially below 375°C., decreases fast with rising temperature. In the region of 375°C. to 425°C., mostly liquid branched aliphatic hydrocarbons are formed. With rising temperature, the quantity of naphthenes, which result, increases gradually. Their share in the liquid products is not considerable at 375°C., but reaches 50 percent at 450° to 460°C. With temperatures of 450° to 500°C., aromatic substances could also be identified in the higher-boiling fractions of the resulting liquid hydrocarbons.

The quantity of gaseous reaction products increases from less than 10 percent at 375°C. to 50 percent of the reaction products at 440°C. The greatest quantity among the single hydrocarbons is that of isobutane. At 450° to 460°C., one-third of the
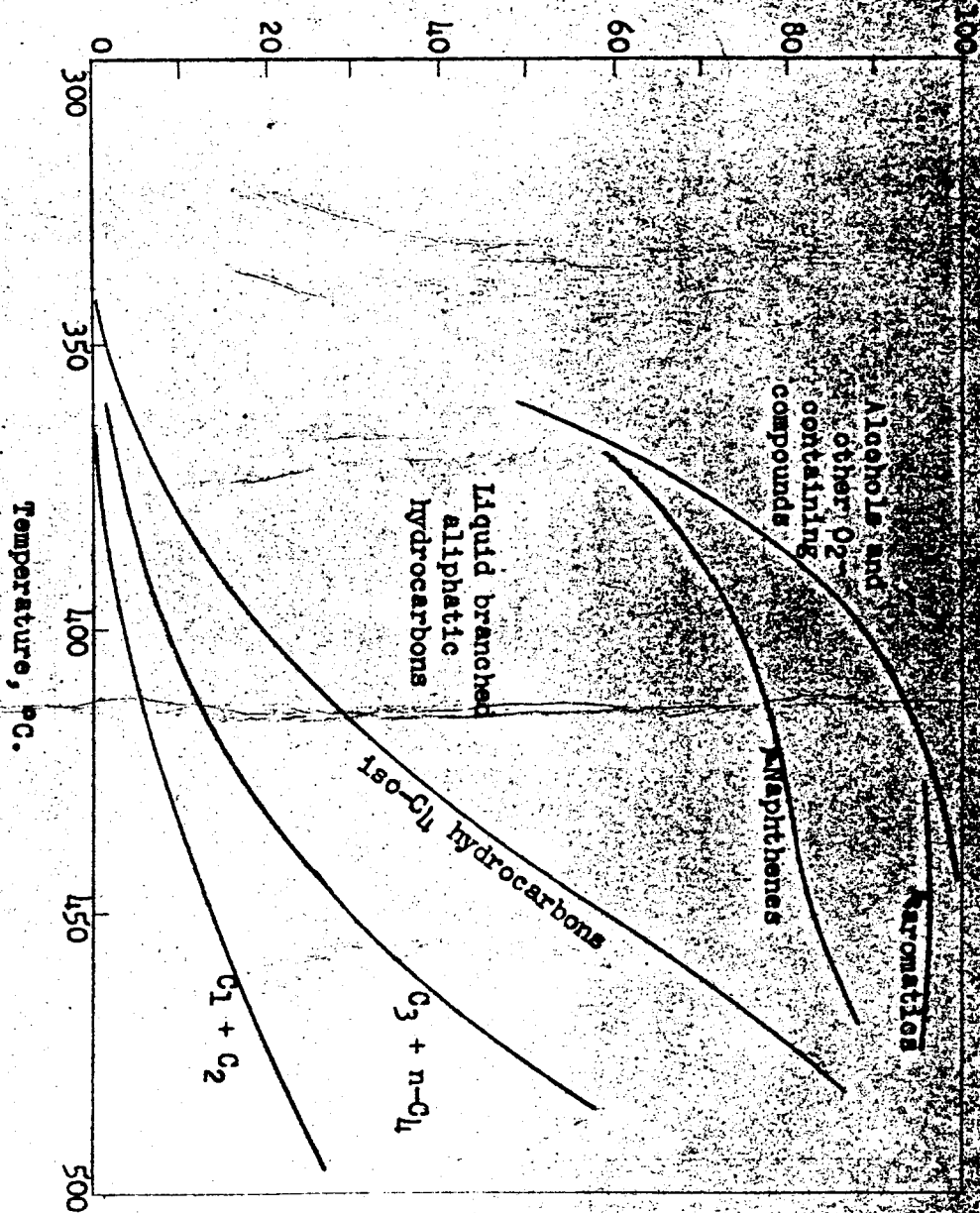
Figure 1.— Composition of the Reaction Products as Dependent on the Synthesis Temperature.

The figure plots composition (%) on the vertical axis (0 to 100) against Temperature, °C. (300 to 500) on the horizontal axis. Curves are labeled:

- Alcohols and other O₂-containing compounds
- Aromatics
- Naphthenes
- Liquid branched aliphatic hydrocarbons
- iso-C₄ hydrocarbons
- C₃ + n-C₄
- C₁ + C₂

butane resulted; for example, in quantities of around 10 percent of the isobutane (0.5 to 3 percent of the total products). The quantity of the normal pentane was only one percent of the liquid hydrocarbons.

Table 1 shows yields of gasoline and gasol after the operation in one stage under different experimental conditions, that is, different pressures and different material of the reaction pipes. With the exception of the last experiment, the temperature was always 450°C.

Table 1.- Yields of Gasoline and Gasol
Under Different Experimental
Conditions.

				Yields, inert-free gas, g./Nm³		
Exp. No.	Pressure, atmos.	Temp., °C.	Material of the reaction pipe	C_3 + n-C_4	i-C_4	Gasoline and gasol
Th 51	0	450	copper	-	-	-
Th 134	6	450	copper	-	-	trace
Th 151	30	450	copper	5.1	5.4	16.1
Th 101	150	450	copper	9.1	30.0	29.7
Th 153	150	450	copper	11.4	21.7	31.3
Th 143	300	450	copper	20.4	41.6	37.4
Th 147	500	450	copper	16.0	46.5	40.5
Th 139	30	450	stainless steel	10.7	10.7	22.6
Th 154	150	430	stainless steel	7.2	13.7	56.6

With atmospheric pressure, no reaction could be observed; with 6 atmospheres, it was insignificant. With 30 atmospheres and a conversion of 22 percent of the CO, 5.1 grams C_3 + n-C_4 hydrocarbons, 5.4 grams i-C_4 hydrocarbons, and 16.1 grams liquid hydrocarbons per normal cubic meter inert-free inlet gas was formed. With rising pressure, the quantity of the products, resulting from one operation, increased. It reached, at 500 atmospheres, 46.5 grams i-C_4 hydro-

carbons was greater when V2A (stainless steel) pipes instead of copper-lined pipes were used.

Figure 2 shows graphically the influence of pressure on the field, obtained at 450°C. in one stage. The yields of liquid hydro-carbons and gasol increase with rising pressure; and, connected with this, with longer stay of the gases within the catalyst space, the conversion of carbon monoxide also increases. This conversion of carbon monoxide can be increased with rising pressures, since the danger of a carbon formation declines with this increase.

With lower pressures, for example 50 to 100 atmospheres, a similar conversion can be obtained, if the operation takes place in several stages instead of one stage, using a pressure of 300 to 500 atmospheres. This means that the necessary catalyst quantity is so much lower that a higher working pressure is chosen.

Figure 3 shows a typical gasol distillation of an experi-ment, which had been carried out with a pressure of 150 atmospheres and a temperature of 450°C. (Th 101a). The main fraction is an iso-butane boiling at -12°C. Isobutene, in the portions boiling between -10° and 5°C., was always tested for by treatment with 64 percent sulfuric acid, but was not formed.

Figure 4 shows the result of a distillation (Th 101a, 150 atmospheres, 450°C.) belonging to the same experiment of the liquid hydrogenized hydrocarbon. In Table 2, the refractive index, the density, the aniline point, and the specific dispersion of the re-sulting single fractions are compiled. Table 3 shows the result
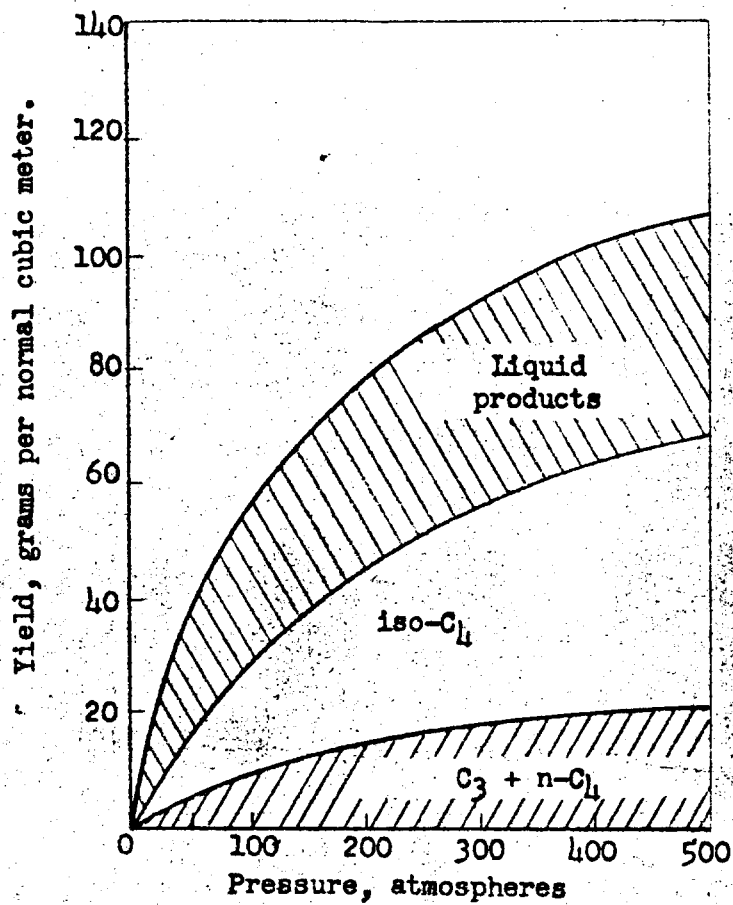
Figure 2.- Influence of Pressure on the
Yield in One Stage.

Temperature, °C.

+ 10

0

- 10

- 20

- 30

- 40

- 50

0   1   2   3   4   5   6   7   8   9   10

Liters

C₃

iso-C₄

C₄

Figure 3.— Gasol Distillation.

Temperature, °C.

0   50   100   150

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30
31
32
33
34

Cubic centimeters.

— Fraction nu

→ 193
→ 239

Figure 4.— Gasoline Distillation of the Experiment Th 101a.

tities of normal paraffins have been obtained. About one percent of the liquid hydrocarbons was n-pentane, but 12 percent was iso-pentane boiling at 28°C.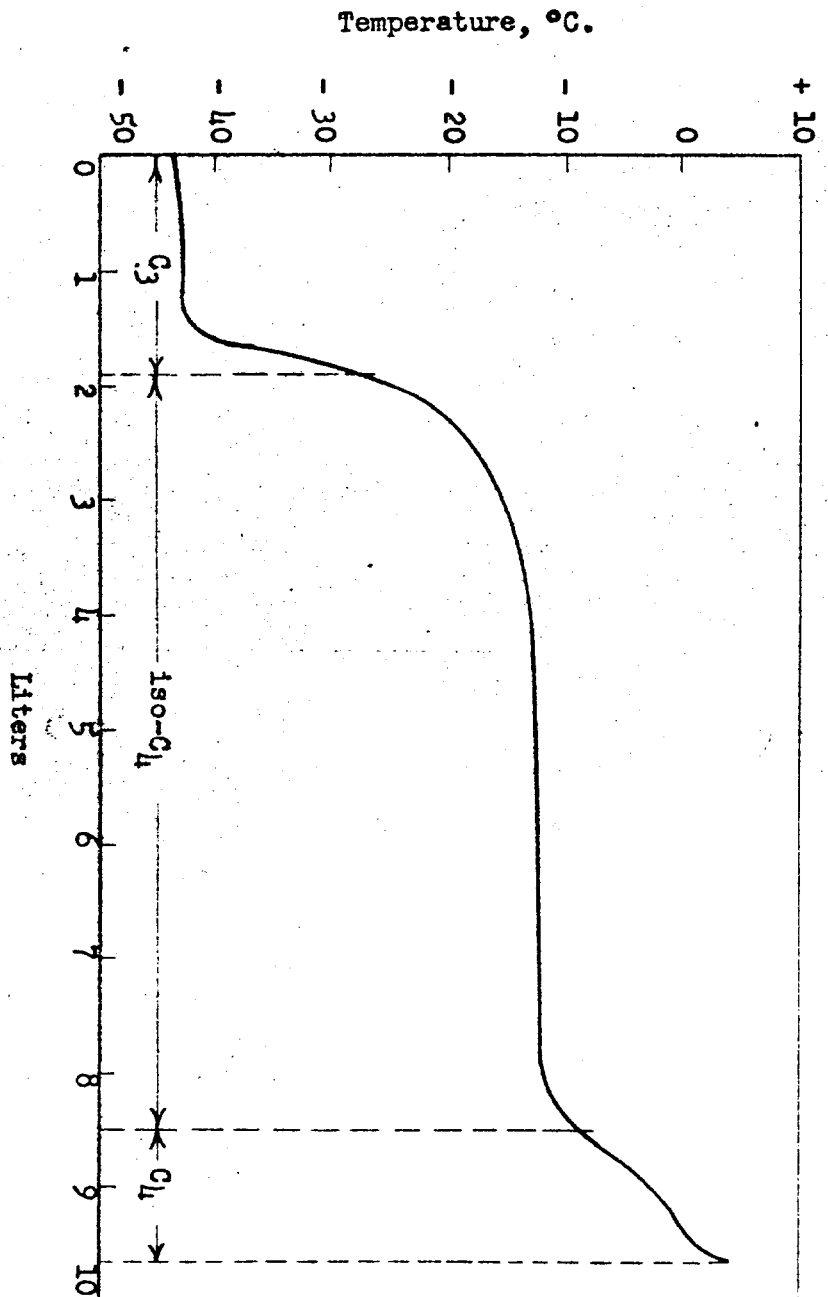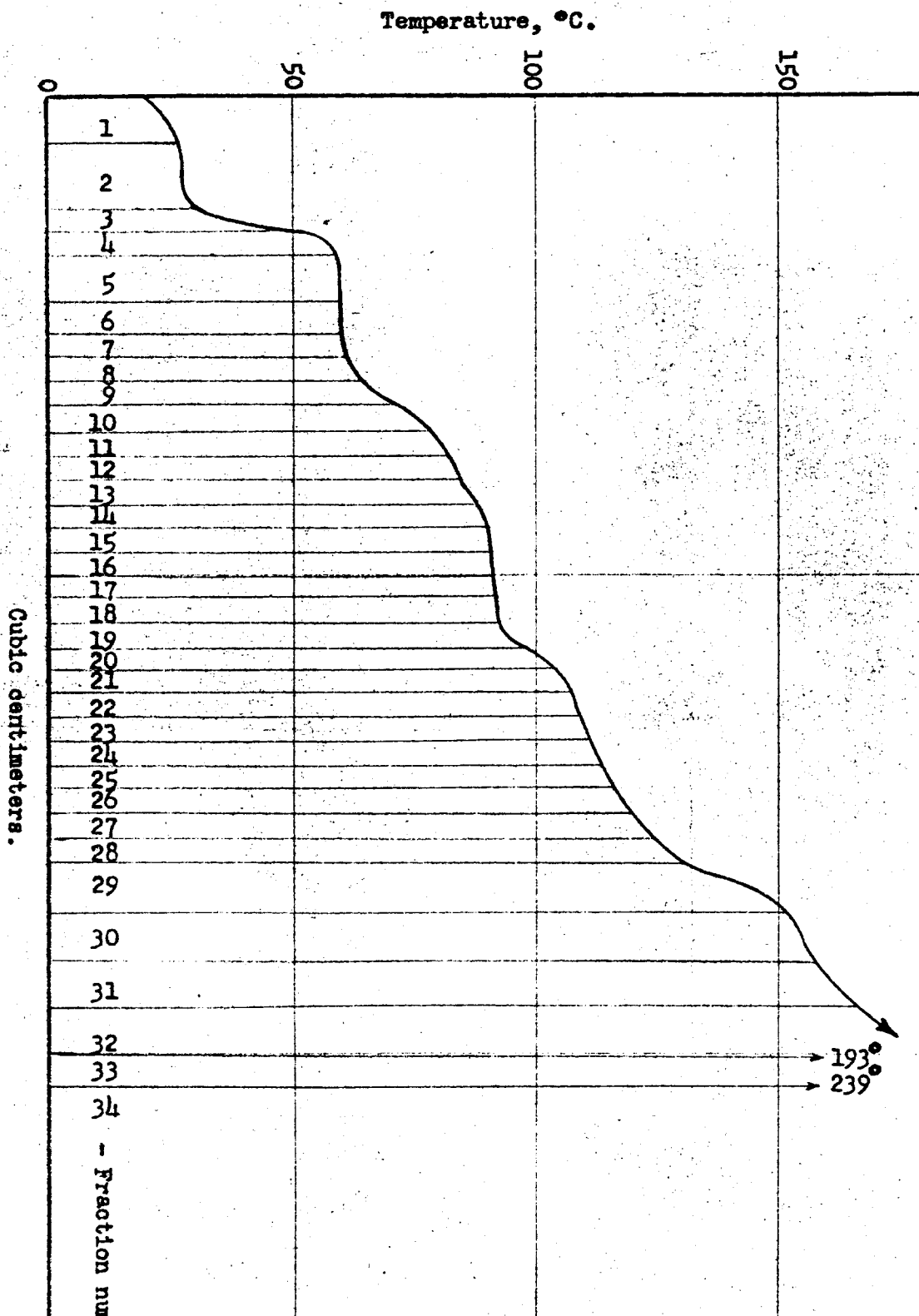 Relatively large quantities consisted of 2-methyl-pentane (13.6 percent) and possibly of 2,4- and 2,2-dimethylpentane. The numbers compiled in Table 2 give us an approximate picture of the composition of the hydrocarbons.

Table 2.- Determination of the single fractions of the liquid reaction product of Experiment Th 101a.

No.	Boiling point, °C.	n_D^{20}	d_4^{20}	Aniline point	Specific dispersion	cm^3
1	20.0—26.9	-	-	-	-	95
2	26.9—30.9	1.3543	-	-	-	140
3	30.9—47.8	1.3580	0.6255	-	-	45
4	50.5—59.4	1.3720	0.6530	-	-	50
5	59.4—60.3	1.3730	0.6556	-	-	100
6	60.3—60.8	1.3730	0.6555	-	-	65
7	60.3—61.4	1.3738	0.6556	-	-	50
8	61.5—63.9	1.3757	0.6600	-	-	50
9	64.2—72.6	1.3849	0.6802	-	-	50
10	72.6—79.0	1.3920	0.6951	58.4	99.6	60
11	79.7—82.2	1.3877	0.6850	68.1	99.7	50
12	82.3—84.5	1.3869	0.6830	71.0	100.0	50
13	84.3—88.4	1.3917	0.6948	65.9	-	50
14	88.6—90.3	1.3979	0.7124	59.8	-	50
15	90.3—90.8	1.4008	0.7210	56.9	-	50
16	90.8—91.0	1.4017	0.7235	56.2	95.4	50
17	91.0—91.4	1.4022	0.7250	55.4	93.1	40
18	91.4—92.7	1.4041	0.7266	53.6	-	60
19	92.7—97.9	1.4078	0.7367	50.4	-	50
20	98.0—104.4	1.4150	0.7500	44.6	-	40
21	104.4—107.6	1.4190	0.7560	44.5	102.0	50
22	107.7—109.5	1.4150	0.7500	50.5	103.7	50
23	109.5—110.9	1.4120	0.7458	55.1	100.2	50
24	110.9—113.2	1.4118	0.7458	56.6	96.9	50
25	113.2—117.0	1.4142	0.7507	55.8	95.9	52
26	117.0—119.5	1.4182	0.7585	52.8	97.3	48
27	119.5—124.3	1.4220	0.7649	50.2	98.3	60
28	124.3—131.3	1.4269	0.7720	47.3	103.1	50
29	142—152	1.4420	0.7940	36.6	119.1	100
30	152—158	1.4449	0.7985	34.6	117.2	100
31	158—167	1.4496	0.8038	30.9	119.7	100
32	167—193	1.4620	0.8235	20.5	128.5	100

Table 3.-- Identified hydrocarbons among the liquid reaction
product of Experiment Th 101a.

Boiling range, °C.	Compound	Percent by volume of the liquid reaction product
20.0—33.0	2-Methylbutane	11.8
33.0—47.8	n-Pentane	~1.0
	2,2-Dimethylbutane	< 0.2
	not identified compound	~0.3
47.8—64.0	2-Methylpentane	13.6
	not identified compound	1.7
64.0—88.5	~23 volume percent naphthene	2.9
	~77 volume percent paraffin	9.6
	(These fractions probably contain greater portions of 2,4-dimethylpentane and 2,2-dimethylpentane)	
88.5—98.0	1,3-Dimethylcyclopentane	9.4
	2-Methylhexane	5.1
98.0—113.0	~68 Volume percent naphthene	7.8
	~32 volume percent paraffin	3.7
113.0-131.3	~76 volume percent naphthene	7.7
	~24 volume percent paraffin	2.4
131.3-239	Naphthene, aromatics, paraffin	22.3
239	Residue (solid)	0.5
		101.0

Figure 5 and Tables 4 and 5 show analogous results for the experiment at 150 atmospheres and 375°C., Th 101b. The products of this experiment are different from those obtained at 450°C. by an essentially lower naphthene content and by a higher content in branched aliphatic hydrocarbons (compare Table 1).

Table 4.- Determination of the single fractions of the liquid reaction product of Experiment Th 101b.

| No.	Boiling point, °C.	n_D^{20}	d_4^{20}	Aniline point	Specific dispersion	cm^3
1	27.4--37.7	1.3641	0.6520	–	115.6	10
2	40.0--59.3	1.3752	0.6558	–	106.0	10
3	59.3--60.5	1.3730	0.6539	–	95.3	10
4	60.5--60.7	1.3729	0.6535	–	95.3	10
5	60.7--62.1	1.3730	0.6548	–	97.3	10
6	62.1--76.7	1.3851	0.6746	55.4	106.9	10
7	76.7--80.2	1.3893	0.6819	61.7	104.6	10
8	80.2--81.2	1.3849	0.6733	72.1	96.8	10
9	81.2--81.3	1.3849	0.6734	72.9	98.9	10
10	81.1--82.0	1.3859	0.6738	71.2	98.8	10
11	82.0--85.4	1.3900	0.6790	64.5	107.2	10
12	85.4--89.8	1.3962	0.6993	58.4	105.4	10
13	89.8--90.9	1.3981	0.7119	59.0	101.8	20
14	90.9--91.4	1.3992	0.7161	57.9	97.6	10
15	91.4--97.3	1.4032	0.7237	52.4	95.6	10
16	97.3--108.6	1.4096	0.7345	52.4	98.8	10
17	108.6--109.8	1.4046	0.7248	63.7	99.5	10
18	109.8--109.9	1.4040	0.7232	65.0	99.6	10.2
19	109.9--114.6	1.4067	0.7283	62.0	97.6	10.3
20	114.6--117.7	1.4147	0.7446	53.5	99.0	10.0
21	117.7--120.0	1.4183	0.7530	51.1	96.8	10
22	120.0--128.0	1.4216	0.7517	49.8	96.6	10
23	145.4--154.4	1.4290	0.7710	55.2	102.2	50
24	154.4--161.9	1.4320	0.7758	52.5	105.7	50
25	161.9--191.4	1.4403	0.7906	51.1	108.9	60
26	191.4--225.0	1.4620	0.8269	39.6	120.0	23
	225	---	---	–	–	10
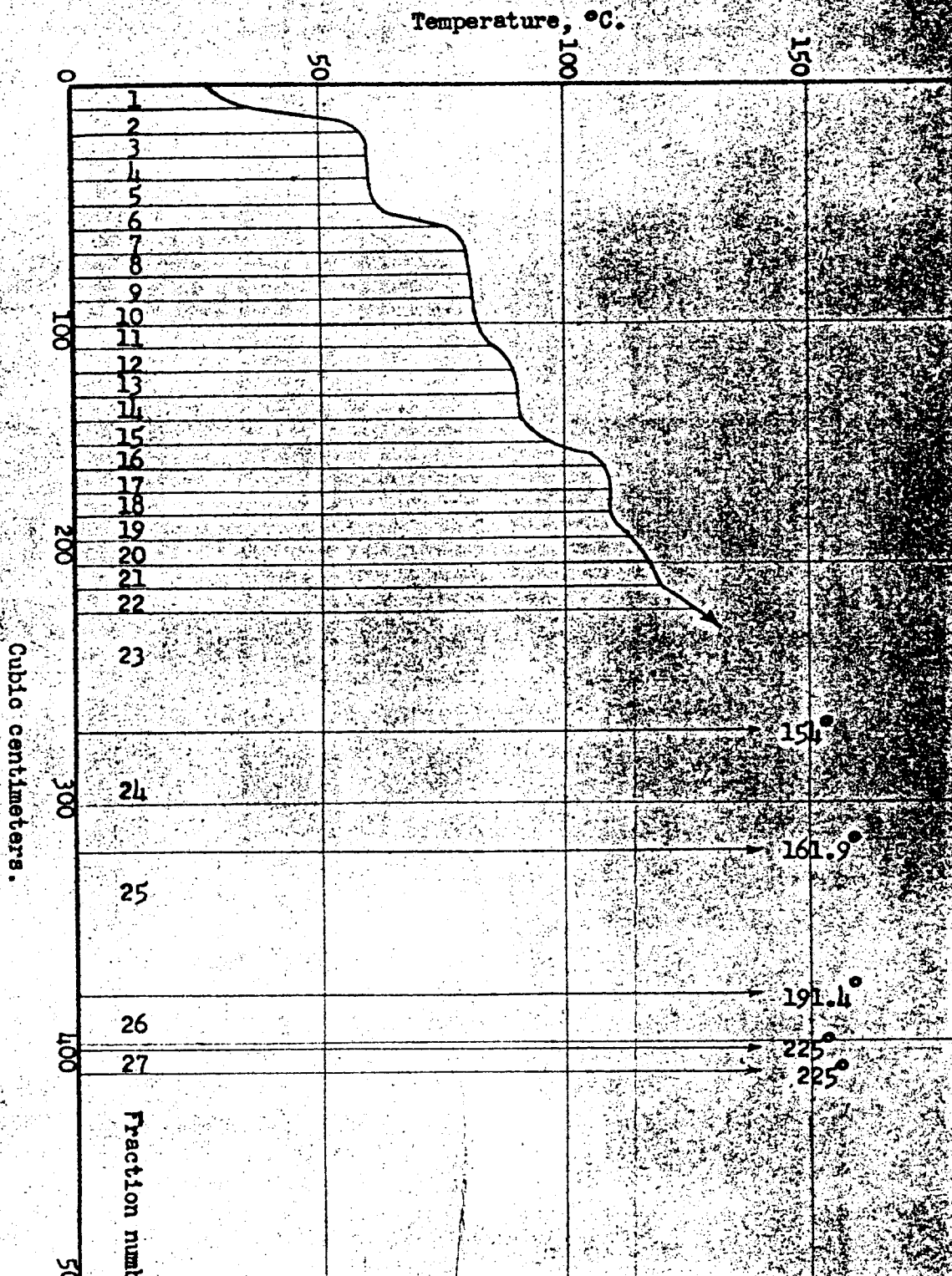
Figure 5.— Gasoline Distillation of the Experiment Th 101b.

Table 5. - Hydrocarbons determined among the liquid
reaction products of Experiment Th 101b.

Boiling range, °C.	Compound	Percent by volume of the liquid reaction product
27.4 - 47.5	Not determined[1]	2.8
47.5 - 73.5	2-Methylpentane	10.9
73.5 - 85.3	2,4-Dimethylpentane	12.3
85.3 - 102.5	2-Methylhexane	6.1
	1,3-Dimethylcyclopentane	6.1
102.5 - 112	2- or 3-fold branched octanes	8.1
112 - 225	uncertain	51.3
225	Residue	2.4

[1] The isopentane fraction was not caught under the liquid products of this distillation.

Table 6 shows a classification of a series of measurements for resistance to knocking by the motor method.

The first seven gasoline samples have been washed with a 30-percent calcium chloride solution before starting the determination. The octane numbers are between 78 and 80, that is, rather independent of the boiling limits. (Compare Experiments 3, 4, and 5.) An unwashed raw product had an octane number 84.5 (Experiment 13).

The samples 8, 9, and 10 have been hydrogenized on a nickel catalyst before testing the octane number. The octane numbers of these are between 83 and 85.7.

The gasoline (11) obtained at 450°C. and 150 atmospheres. and hydrogenized before testing the resistance to knocking, after

Table 6.- Resistance to knocking of different gasolines obtained in the isosynthesis.

Experiment No.	Pressure, atmos.	Temp., °C.	Boiling range, °C.	Washed with 30-percent CaCl2 solution	Vapor pressure, according to Reid	Hydro-genized	Tetra-ethyl lead, percent by volume	Motor octane number
Th 64	30	500	up to 150	+	0.70	-	-	79.5
Th 101a	150	450	up to 150	+	0.54	-	-	78.0
Th 101a	150	450-475	30-150	+	0.45	-	-	80.0
Th 101a	150	450-475	30-165	+	0.42	-	?	79.5
			(total product)					
Th 101a	150	450-475	70-150	+	0.16	-	-	76.8
Th 101b	150	375	up to 150	+	0.75	-	-	79.0
Th 159	150	370	up to 150	+	0.71	-	-	80.5
Th 64	30	500	up to 150	+	0.40	+	-	84.0
Th 101a	150	450	up to 150	+	0.53	+	-	65.7
Th 159	150	370	up to 150	+	0.41	+	-	83.0
Th 101a	150	450	up to 150	+	0.53	+	0.08	95.0
Th 159	150	370	up to 150	+	0.41	+	0.08	89.6
Th 159	150	370	up to 150	?	0.75	?	-	84.5

Conclusion

Operating with thorium catalysts and in one stage, 110 grams gasol, gasoline and oil, could be obtained per normal cubic meter inert-free inlet gas. Operating in two or more stages, it should be possible to increase the yield still more.

The composition of the reaction products could be varied within large limits by the choice of the synthesis conditions. For example, the yields of isobutane could be increased from about 5 grams per normal cubic meter, when we operated for the highest yield in liquid products to 50 grams per normal cubic, when we operated with a corresponding lower yield in liquid hydrocarbons. With the precise knowledge of the influence of the catalyst composition, it will be possible to favor in a much higher degree the formation of certain desired hydrocarbons.

The octane numbers of the resulting gasoline, after a hydrogenation and an addition of 0.08 volume percent tetraethyl lead, were up to 95. By using the resulting isobutane for the production of alkylation gasoline, the mixtures of both gasolines could be improved to octane numbers of 100 and over.

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