

EFFECT OF PRESSURE VERSUS CONTACT TIME UPON CONVERSION

The explanation for the increases in conversion and in hydrocarbon yields that result from rise in pressure appears to be the prolonged contact time associated with higher pressures. Two series of experiments were undertaken to determine whether this is actually the case or whether high pressure is in itself a necessary condition for high conversion. In the first group of experiments, conducted with a thoria catalyst, a pressure of 150 atmospheres was maintained, and the contact time was varied by decreasing the throughput in a ratio of 1:½:¼. In the second group, a constant throughput was maintained, and the contact time was increased by the operating pressure. The results of the two groups of experiments, summarized in table 6, show that increase in pressure caused a greater increase in conversion than a large increase in contact time at constant pressure. At a constant pressure of 150 atmospheres, conversion was somewhat increased by prolonging the contact time. However, at higher pressures, for example 600 atmospheres, carbon monoxide conversion was considerably higher than at lower pressures in spite of the smaller increase in contact time. Comparison of experiments 3 and 5 shows that weight of carbon monoxide converted at 600 atmospheres was eight times that converted at 150 atmospheres.

The results obtained in the tests summarized in table 6 are substantiated by the fact that almost no carbon monoxide-hydrogen conversion is obtained at atmospheric pressure, even at a very low throughput of synthesis gas (for example, ⅓ at the usual throughput). This can very probably be explained in terms of the equilibrium conditions that govern the primary reaction.

TABLE 7.—Effect of type of operation with ThO_2 catalystA.—Effect of 2-stage operation at 30° C., 150 atmospheres, $\text{CO:H}_2=43.1:48.6$

Type of operation	Space velocity ^a	Contraction, percent	CO conversion, percent	Usage ratio, CO:H_2	Ratio $\text{CO}_2:\text{H}_2\text{O}$ (moles)	Yields, g./m ³ ^b			Distribution, weight percent of total hydrocarbons				
						CO_2	H_2O	Total hydrocarbons	C_1+	$i-\text{C}_4$	C_2+nC_4	C_5+C_6	
Converter:													
I.....	11.4	28	55	1.29:1	3.42:1								
II.....	13.7	27	50	1.2:1	3.77:1	206	24.6	72.9	45.2	25.8	14.5	34.5	
I and II.....	6.0	45	75	1.05:1	2.47:1	194	21.0	67.9	49.8	27.8	11.2	11.7	
						265	44.0	111.3	35.6	32.4	14.8	17.7	

B.—Effect of recycle operation at 475° C., 30 atmospheres, $\text{CO:H}_2=43.3:48.0$

Recycle:	Space velocity ^a	Contraction, percent	CO conversion, percent	Usage ratio, CO:H_2	Ratio $\text{CO}_2:\text{H}_2\text{O}$ (moles)	CO_2	H_2O	Total hydrocarbons	C_1+	$i-\text{C}_4$	C_2+nC_4	C_5+C_6
Without.....	11.4	20	40	1.14:1	3.74:1	162	17.8	51.9	22.0	18.3	25.1	24.1
With.....	12.4	29	32	1.67:1	4.41:1	73	67.4	52.6	35.8	26.2	19.2	18.8

^a Liters in-gas per 28 g. ThO_2 per hour.
^b G./m³ inert-free feed gas.

^c Recycle ratio fresh feed gas: recycle gas=1:6.

TABLE 6.—Effect of pressure versus contact time on isosynthesis

Experiment No.	Pressure, atmospheres	Feed gas, l./hr.	End gas, l./hr.	Contraction, percent	Average relative contact time	CO conversion, percent
1.....	150	13.4	10	25	1.0	46
2.....	150	7.0	5	28	1.96	53
3.....	150	3.6	2.5	30	3.85	58
4.....	300	15.9	10	37	1.74	66
5.....	600	20.4	10	51	2.87	83

EFFECT OF TWO-STAGE AND RECYCLING OPERATIONS

Part A, table 7, summarizes the results obtained when two converters were operated in a single stage with standard thoria catalyst at 150 atmospheres and 450° C. (rows 1 and 2) and when the two converters were operated in series (row 3). Comparison of the data in the first two rows with experiment 1, table 6, shows that the catalysts used for the experiments in table 7 were somewhat more active. Other conditions were similar.

Liquid products were removed between stages I and II at a pressure of 150 atmospheres and at a temperature of -25° C. The total contraction for converters I and II operated in series was 45 percent, and carbon monoxide conversion was 75 percent. Comparison of this "two-stage" experiment with experiment 2, table 6, in which the gas throughput per weight of catalyst was approximately the same, shows that conversion is considerably higher for operation in two stages with intermediate removal of the reaction products. As was to be expected from the increased hydrogen consumption in the two-stage procedure, the formation of gaseous hydrocarbons is somewhat higher in the latter than in single-stage operation. Comparison of the results in table 7 with those in table 5 shows

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that, for approximately the same contact time, operation in two stages at 150 atmospheres produced about the same total yield as operation in a single stage at 300 atmospheres. It should be noted, however, that at 300 atmospheres the weight of synthesis gas passed per unit of time and unit weight of catalyst was twice that passed at 150 atmospheres.

A second two-stage experiment was carried out at 150 atmospheres with carbon monoxide-rich gas (48.6 percent carbon monoxide and 41.7 percent hydrogen). In this experiment, the temperature was no longer the same for both stages (stage I, 430° C.; stage II, 470° C.). This had the effect of distributing conversion more equally between the two converters. The total hydrocarbon yield was 125.7 grams (37.6 percent liquids, 26.8 percent iso-C₄ hydrocarbons) per cubic meter inert-free feed gas.

In the recycle experiments (apparatus shown in fig. 5), the synthesis gas was repeatedly passed over the same catalyst. After each passage, the liquid reaction products and the less volatile gaseous hydrocarbons were removed in a pressure separator at -25° C. Fresh feed gas was continuously added at the converter inlet, and a portion of the gas was removed as tail gas at the condenser outlet. The amount of outlet gas corresponded to that used in standard experiments, that is, about 10 liters per 28 grams of thorium oxide per hour. The recycle ratio, that is, the ratio of the amount of fresh feed gas to the recycle throughout, was 1:6. Part B, table 7 contains the results for an experiment of this type carried out at 30 atmospheres. The results for a similar experiment without recycle are shown for comparison. It will be seen that recycling decreased carbon monoxide consumption and increased the consumption of hydrogen. More water and a larger liquid hydrocarbon fraction were obtained, although the total hydrocarbon yields were approximately the same for both methods.

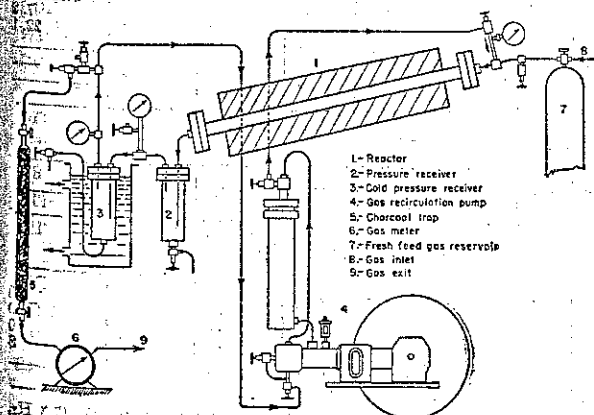


FIGURE 5.—PRESSURE APPARATUS FOR RECYCLING EXPERIMENTS.

Operation in more than one stage with intermediate removal of the reaction products makes it possible to obtain extensive carbon monoxide conversion at moderate pressures. On the other hand, the recycle process offers a means of varying the conversion ratio of carbon monoxide and hydrogen over a relatively wide range.

EFFECT OF PROMOTERS AND CARRIER ON THE ACTIVITY OF THORIUM OXIDE

The following experiments with catalysts consisting of more than one component were made to determine which compounds were suitable as promoters for thorium and to determine whether any multicomponent catalyst could be substituted satisfactorily for thoria. The effect of adding alkali was interesting because of its influence in increasing the higher molecular-weight fractions of products from the normal hydrocarbon synthesis when present in small amount in iron catalysts. The addition of alkali to the catalysts used in the synthesis of alcohols from carbon monoxide and hydrogen has a similar effect in favoring the production of higher alcohols, especially iso-butyl alcohol. As it is known that under certain conditions phosphoric acid converts unsaturated hydrocarbons such as propene and n-butene to higher branched hydrocarbons, particularly to the dimers, the effect of the addition of phosphoric acid also was examined.

It is possible that the branched-chain hydrocarbons are produced by way of alcohols and dimethylether, thorium oxide catalyzing the formation of oxygenated compounds and their subsequent dehydration, as well as the conversion of the resulting unsaturated hydrocarbons to saturated compounds having the same or a larger number of carbon atoms. In this connection, two types of compounds were added to thorium oxide, one designed to promote formation of alcohol and the other to increase the activity of thorium oxide as a dehydrating agent for alcohols. A series of experiments was made with catalysts containing constituents known to have these properties (for example, zinc oxide-aluminum oxide catalyst).

Other substances also were tested. Thus, cerium was added to thorium oxide; thorium itself was replaced by decomposed and reprecipitated monazite sand; copper, iron in decreasing amounts, and alkaline earths such as magnesium, manganese, etc., also were added to thorium oxide.

EFFECT OF ALUMINA

The following thoria-alumina catalysts were tested:

1. ThO₂-Al₂O₃ prepared by coprecipitation of both components.

2. Al_2O_3 and ThO_2 prepared separately and tested in series in the same reactor.

3. ThO_2 and Al_2O_3 precipitated and washed separately, and the moist precipitates then mixed thoroughly and dried.

4. ThO_2 - Al_2O_3 -kieselguhr.

COPRECIPITATED ThO_2 - Al_2O_3

A typical catalyst in this group, containing 20 percent aluminum oxide (based on the thorium oxide content), was prepared as follows: To a solution of 240 grams of thorium nitrate and 169 grams of aluminum nitrate dissolved in 2 liters of distilled water and heated to boiling was slowly added a boiling solution of 167 grams of sodium carbonate in 2 liters of water. The precipitated mixture was boiled for a short time, filtered, and washed with boiling distilled water (15 portions of 400 cubic centimeters each). The precipitate was then dried at 110°C . and treated in a current of air at 300°C .

In table 8, part A, are summarized the data obtained with catalysts whose aluminum oxide content was, respectively, 0, 10, 20, and 40 percent, based on the thorium oxide content. These tests showed the following effects of the presence of aluminum oxide: (a) The optimum amount of alumina was 20 percent; (b) the presence of alumina in the catalyst had no

appreciable effect upon carbon monoxide conversion at any one temperature. It did, however, increase hydrogen conversion. Increased formation of methane and C_2 hydrocarbons and a decreased yield of liquid hydrocarbon and oil-soluble alcohols were observed. The amounts of C_2 and C_3 hydrocarbons also decreased in the presence of aluminum oxide, whereas the amounts of water-soluble alcohols (chiefly methanol) remained approximately the same. The isohydrocarbon content of the C_4 fraction also appeared to be independent of the aluminum oxide content; (c) it is interesting to note that the formation of unsaturated compounds was higher at the lower temperature. The isobutene content of the C_4 fraction was 6 percent at 475°C ., 18 percent at 450°C ., and 46 percent at 425°C .; (d) increased temperature and pressure increased the carbon monoxide conversion and the iso- C_4 yield. Thus, pressures between 300 and 600 atmospheres and temperatures between 450°C . and 475°C . were optimum.

SEPARATE ThO_2 AND Al_2O_3 LAYERS IN THE SAME REACTOR

The experiments described above showed that an increase in the aluminum oxide content up to 20 percent, based on ThO_2 , produced a noticeable increase in iso- C_4 hydrocarbon yields.

TABLE 8.—Effect of Al_2O_3 on ThO_2 catalyst in isosynthesis with $1\text{CO}:1\text{H}_2$ gas (catalyst pretreated by sintering in air at 300°C .) (throughput, 10 liters outlet gas/28 g. ThO_2 /hr.)

Al ₂ O ₃ percent of ThO ₂	Temperature, °C.	Pressure, atmospheres	Conversion, percent		Yields, g./m ³ gas (CO+H ₂)										i-C ₄ , percent of total C ₄	i-C ₄ H ₈ , percent of total i-C ₄	OH:O ₂ H ₂
					Hydrocarbon products						Alcohols, soluble in—		Total liquids plus gasol				
					CO	H ₂	C ₁ +	i-C ₄	n-C ₄	C ₂	C ₃	C ₄		Oil			
0	450	300	61	47	42.2	22.7	3.2	10.9	4.2	11.1	8.6	10.7	98.3	88	8		
0	475	300	68	61	39.6	27.3	3.8	21.5	14.2	12.9	4.6	5.0	101.8	88	5		
10	450	300	59	51	32.8	37.6	5.4	5.5	2.7	13.2	3.3	12.6	97.2	87	10		
10	475	300	68	62	22.5	50.4	9.8	10.2	3.5	21.3	2.5	10.2	105.6	83	3		
20	450	300	64	60	21.0	47.2	6.1	4.8	2.2	26.9	1.2	11.8	92.1	89	4		
20	450	600	78	67	19.2	58.7	3.5	7.0	28.1				105.9	94	2		
20	450	1,000	85	81	27.3	54.6	9.3	14.7	38.9				113.7	86	5		
40	425	300	56	50	32.7	26.6	4.1	1.4	12.0	5.1	3.1	24.5	92.4	87	46		
40	450	300	65	59	35.1	35.1	6.5	5.1	9.7	20.2	.6	14.5	97.9	85	18		
40	475	300	64	60	18.3	43.0	5.6	10.8	13.0	22.0	.5	3.9	81.7	88	6		

A.— ThO_2 - Al_2O_3 coprecipitated

B.— ThO_2 + Al_2O_3 in two successive layers																
20	450	300	70	62	48.0	27.1	5.2	15.5	7.4	24.5	2.0	2.9	100.7	84	5	

C.— ThO_2 - Al_2O_3 precipitated separately and mixed in wet state

	Temperature, °C.	Pressure, atmospheres	Conversion, percent		Yields, g./m ³ gas (CO+H ₂)										i-C ₄ , percent of total C ₄	i-C ₄ H ₈ , percent of total i-C ₄	OH:O ₂ H ₂
			CO	H ₂	C ₁ +	i-C ₄	n-C ₄	C ₂	C ₃	C ₄	Oil	H ₂ O	Total liquids plus gasol				
20	400	300	49	49	19.0	17.0	4.0		4.0	7.0	1.0	8.0	49.0	81	11		
20	450	300	73	67	34.1	60.5	9.0	8.6	10.2	14.8	1.0	2.3	115.5	87	8		
20	475	300	78	77	25.9	69.0	8.0	9.8	8.6	27.9			113.2	90	2		
20	450	600	82	82	56.4	61.3	6.6	5.5	5.4	17.4	1.0	3.0	133.8	91	6		
20	425	300	56	57	24.6	17.6	8.6	5.4	6.4	42.7	.3	3.0	59.8	67			

* This catalyst was precipitated from somewhat more dilute solutions than the preceding catalysts.

^b $\text{CO}:\text{H}_2 = 49:41$.

^c Al_2O_3 precipitated from sodium aluminate.

^d Composition of product gas in this experiment was the following,

in percent by volume: 37.7 CO_2 , 0.7 olefin, 0.1 O_2 , 18.2 CO , 17.3 H_2 , 12.1 hydrocarbons, C-No. 2.4, 14.9 N_2 .

* This catalyst contained also 10 percent kieselguhr, based on ThO_2 , which was added to the mixture of wet precipitates.

¹ $\text{CO}:\text{H}_2 = 51:39$.

It was of interest to determine whether similar results could be obtained when aluminum oxide was used in a separate layer, placed immediately after the thorium oxide layer. Both catalysts were prepared by precipitation with sodium carbonate.

Table 8, part B, summarizes the results obtained for an experiment at 300 atmospheres and 450° C., with a catalyst containing 29 percent aluminum oxide based on thorium oxide content. Comparison with part A shows that the results were most similar to those obtained with the standard (aluminum-free) thoria catalyst, particularly with respect to the liquid hydrocarbon and iso-C₄ yields. The alcohol yield was small and the methane yield large.

ThO₂-Al₂O₃ PRECIPITATED SEPARATELY AND MIXED IN WET STATE

In these experiments, thoria was precipitated from the nitrate solution with sodium carbonate; aluminum oxide was precipitated from an aluminate solution with sulfuric acid. After washing, the two precipitates were combined in measured amounts, mixed thoroughly, and dried. The preparation of a catalyst containing 20 percent aluminum oxide, based on thorium oxide, is described below:

Two hundred and forty grams of thorium nitrate in 2 liters of distilled water was heated to boiling and precipitated, with a boiling solution of 95 grams of sodium carbonate in 2 liters of water. The precipitate was filtered and washed with boiling distilled water (15 portions of 400 cubic centimeters). 169 grams of aluminum nitrate in 1 liter of water was heated to boiling and treated with 77 grams of sodium hydroxide in 500 cubic centimeters of water. The sodium aluminate solution was heated to boiling and treated with 17.2 cubic centimeters of concentrated sulfuric acid in 350 cubic centimeters of distilled water. The reprecipitated aluminum hydroxide was suspended and washed by decantation 12 times with 1-liter portions of water. The precipitate was filtered with suction and washed on the filter with boiling distilled water (3 portions of 400 cubic centimeters). The thorium and aluminum precipitates were made into a slurry in hot water, stirred, and evaporated on the water bath with constant stirring. The product was dried, first at 110° C. and then in a current of air of 300° C.

It will be seen from part C, table 8, that this type of catalyst, operated at 450° to 475° C. and at 300 to 600 atmospheres, produced exceptionally good yields of iso-C₄ hydrocarbons and only very small amounts of alcohols.

ThO₂-Al₂O₃-KIESELGUHR

A catalyst containing 20 percent of aluminum oxide and 10 percent of kieselguhr based on the

thorium oxide content was tested at 300 atmospheres pressure. This catalyst was prepared by precipitating the two oxides separately and adding kieselguhr to a mixture of the wet precipitates. It showed an unusually high tendency to form methane and consequently could not be operated at the temperature of 450° C. usually used for the ThO₂-Al₂O₃ catalysts. Operation at 425° C. produced the yields shown in the last row in part C, table 8. The total liquids-plus-gasol yield was low, and the methane production was high, even at the low synthesis temperature of 425° C. A comparatively large proportion of n-C₄ hydrocarbons—one-third of the total C₄ hydrocarbon fraction—was produced.

SUMMARY OF ThO₂-Al₂O₃ EXPERIMENTS

Thoria containing alumina is a valuable catalyst for the isosynthesis, especially where high yields of iso-butane are required. The best results were obtained with catalysts that contained 20 percent aluminum oxide based on thorium oxide. Simultaneous precipitation of the oxides was not necessary. Catalysts prepared by separate precipitation and subsequent mixing of the washed precipitates produced the highest iso-C₄ yields. The use of kieselguhr as a carrier was not desirable.

The principal results obtained for thorium oxide-aluminum oxide catalysts prepared by different methods are summarized in table 9.

EFFECT OF ALKALI ON ThO₂ CATALYST

The oxide was precipitated by the standard procedure and was washed on the filter. It was suspended in water, and various amounts of potassium carbonate in aqueous solution were added. The mixture was then evaporated to dryness, and the resulting product was dried at 110° C.

A series of comparative experiments was carried out at 30 atmospheres and different temperatures with catalysts containing 0, 0.5, 1, 5, and 25 percent potassium carbonate. The gas throughput was 10 liters of outlet gas per hour per 28 grams of ThO₂ in all cases.

Figure 6 shows the effect of the alkali content upon the activity of the ThO₂ catalyst at 450°, 475°, and 500° C. All three curves show that the activity of the thorium oxide catalyst falls off as the alkali content increases. This effect is more marked at the lower temperatures. Thus, at 450° C., conversion dropped from 13 percent to 0 when the alkali content was increased from 1 to 5 percent; at 475° C. it fell from 20 to 3 percent; whereas, at 500° C. it dropped from 28 to 22 percent. The yields of low-boiling and gaseous hydrocarbons decreased more rapidly than those of higher hydrocarbons.

TABLE 9.—Summary of results from $ThO_2-Al_2O_3$ catalysts (300 atmospheres)

Al ₂ O ₃ in catalyst, percent of ThO ₂	Method of precipitation	Synthesis temperature, °C.	Yields, g./m ³ inert-free gas			
			C ₃ +hydrocarbons+gasol	C ₅ +hydrocarbons	i-C ₄	Alcohols
0		450	79.0	42.2	22.7	19.3
0		475	92.2	39.6	27.3	9.6
20	Simultaneous	450	79.1	21.0	47.2	13.0
20	do	475	93.7	17.6	54.8	4.0
20	Separate	450	112.2	34.1	60.5	3.3
20	do	475	112.7	25.9	69.0	3.3
20 ^a	do	425	56.2	24.6	17.6	4.9
29	Separate (two layers)	450	95.8	48.0	27.1	4.9

^a This catalyst contained also 10 percent kieselguhr, based on ThO₂, which was added to the mixture of wet precipitates.

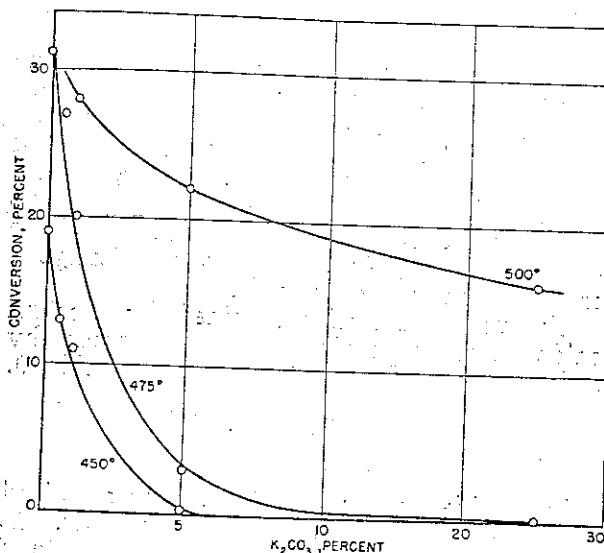


FIGURE 6.—INFLUENCE OF ALKALI CONTENT OF A THORIA CATALYST IN THE ISOSYNTHESIS (30 ATMOSPHERES, VARIOUS TEMPERATURES, EQUAL THROUGHPUT).

Owing to the decreased catalytic activity resulting from the addition of alkali in amounts greater than 1 percent the synthesis can be carried out at relatively high temperatures without extensive formation of methane. In this way it becomes possible to operate in the temperature range in which cyclic hydrocarbons are the principal synthesis products. Thus, when a thorium oxide catalyst containing 1 percent potassium carbonate was operated at 30 atmospheres and 500° C., it produced liquid hydrocarbons containing 42 percent naphthenes, 8 percent aromatics, principally toluene, and 3 percent phenol.

Table 10, row 2, summarizes the data for an experiment with a very weakly alkalinized thorium catalyst (0.6 percent K₂CO₃ based on ThO₂); the results from an alkali-free catalyst are shown for comparison (row 1). These catalysts were operated at 300 atmospheres and 450° C. In both cases, 62 percent carbon monoxide conversion was obtained. Addition of alkali increased the amount of liquid hydrocarbons and of higher alcohols (principally

TABLE 10.—Effect of alkali on ThO_2 , Al_2O_3 , and $ThO_2-Al_2O_3$ catalysts in isosynthesis with 49 CO/H₂ gas at 300 atmospheres pressure and 450° C.

(10 liters outlet gas/28 g. ThO₂ (25 cc.)/hr.)

No.	Catalyst			Conversion, percent	Yields, g./m ³ inert-free feed gas												
	Composition, parts by weight				Hydrocarbon products							Alcohols soluble in—		Total liquids plus gasol	i-C ₄ , percent of total C ₄	i-C ₄ -H ₁₀ , percent of total C ₄	
	ThO ₂	Al ₂ O ₃ ^a	K ₂ CO ₃ ^b		CO	H ₂	C ₃ +	i-C ₄	n-C ₄	C ₃	C ₂	C ₁	Oil				H ₂ O
1	100	0	0	62		42	23	2	11	4	11						
2	100	0	0	62		65	12	1	6	1	6						
3	100	20	0	73		34	61	9	9	10	15	9	11	69	90		
4	100	20	0	67		35	67	10	0	9	16	0	5	112	92		
5	100	20	.2	72		68	78	10	0	9	16	0	2	116	87		
6	100	20	.6	78		75	85	10	0	7	22	0	1	113	87		
7 ^d	0	100	0	70		24	42	51	7	18	6	2	4	120	90		
8 ^d	0	100	.3	25		14	24	10	4	0	9	1	0	124	88		
						24	24	2	0	8	14	<1	<1	35	63		
														28	67		

^a Al₂O₃ precipitated separately from the aluminate in all experiments.
^b Based on ThO₂ content.
^c Alkali added to the washed thoria precipitate, instead of the washed alumina precipitate.

^d Throughput 10 l. outlet gas/25 cc. catalyst/hr.
^e Based on Al₂O₃ content; 0.6 percent K₂CO₃ in catalysts 5 and 6 was equivalent to 3 percent based on Al₂O₃ content.

iso-butyl alcohol). The yields of lower hydrocarbons (C_1 - C_4) and of methanol decreased. These results substantiate those obtained in the normal hydrocarbon synthesis: Large amounts of alkali inhibit the activity of the thorium catalyst; small amounts of alkali promote the formation of higher molecular compounds.

ON ThO_2 - Al_2O_3 CATALYST

Observations made in operating certain thorium oxide-aluminum oxide catalysts, where the aluminum oxide retained some of the alkali used as precipitant, suggested the desirability of a detailed study of the effect of alkali on thorium oxide-aluminum oxide catalysts. In the preparation of this series of experiments, the alkali was added to the washed precipitate obtained from the aluminate solution, except in one experiment in which the alkali was added to the washed thoria precipitate.

Table 10, rows 3 to 6, summarizes the experiments conducted with 100 thorium oxide-20 aluminum oxide catalysts containing 0, 0.2, and 0.6 percent K_2CO_3 based on ThO_2 . The catalyst in row 5 produced the highest iso- C_4 hydrocarbon yield. Iso-pentane (2-methylbutane) comprised 30 to 50 percent of the liquid reaction products. Thus, in this experiment about 100 grams of iso- C_4 and iso- C_5 hydrocarbons were produced per cubic meter of inert-free carbon monoxide-hydrogen mixture. When the alkali was incorporated into the thoria precipitate, higher C_5+ hydrocarbon and much lower C_4 hydrocarbon yields were observed. Nonalkalized and alkalinized alumina catalysts (rows 7 and 8, table 10) containing no thoria were very poor catalysts for the isohydrocarbon synthesis.

EFFECT OF ZINC OXIDE

ON THORIA CATALYST

These catalysts were usually coprecipitated with sodium carbonate. The inverse precipitation procedure (that is, nitrate added to precipitant) produces exceptionally high yields of liquid hydrocarbons. Zinc oxide alone (row 1, table 11), when tested at 300 atmospheres and $450^\circ C$., produced chiefly considerable quantities of methane and alcohols. The experiments summarized in rows 2 to 8 show the effect of precipitation procedure, carbon monoxide:hydrogen ratio in the synthesis gas, and synthesis temperature and pressure. The high thoria content in catalyst 8 resulted in smaller alcohol yields. Thorium oxide-zinc oxide (3:1) catalyst produced a high liquid hydrocarbon yield of 79 grams per cubic meter of inert-free synthesis gas and about 19 grams of iso- C_4 hydrocarbons in a test at 300 atmospheres and $450^\circ C$. (row 9, table 11). The catalyst used for this experiment was prepared as follows:

120 grams of thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, and 74 grams of zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$, were dissolved in 2 liters of distilled water. The solution was heated to boiling and stirred into a boiling solution containing 86 grams of sodium carbonate in 1 liter of distilled water. The precipitate was filtered with suction, washed on the filter with water (15 portions of 400 cc. each), and dried at $110^\circ C$. The bulk density for 2 to 4 mm. granules was 0.75; after heating in a current of air at $300^\circ C$., the bulk density was 1.09.

The catalyst in row 10, table 11, was prepared in the same way; it produced similar C_5+ hydrocarbon and i- C_4 hydrocarbon yields. When the catalyst was precipitated from more dilute solution (for example, 86 grams of sodium carbonate in 2 liters of water), larger amounts of gaseous hydrocarbons and smaller liquid hydrocarbon yields were observed (row 11, table 11). The activity of this catalyst was not as constant as that in the two preceding experiments.

An important advantage of the thorium oxide-zinc oxide catalyst is that in addition to promoting the formation of liquid reaction products they show no tendency to produce carbon deposits. Even after prolonged operation, their color remained pale gray.

ON ALUMINA

Although neither aluminum oxide nor zinc oxide alone is a satisfactory catalyst for the isosynthesis, each is a promoter for the thorium oxide catalyst, the alumina in increasing the production of gaseous hydrocarbons, particularly iso-butane, and the zinc oxide in increasing the yield of liquid hydrocarbons. It was of interest to determine the catalytic activity of an aluminum oxide-zinc oxide preparation because of the desirability of finding a satisfactory substitute for thorium oxide.

An aluminum oxide-zinc oxide (mole ratio 1:1) catalyst was prepared as follows: A solution of 187.5 grams of aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, and 74.5 grams of zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$, in 2 liters of water was heated to boiling and stirred into a boiling solution of 117 grams of sodium carbonate dissolved in 2 liters of water. The slurry thus obtained was again heated to boiling. Then the precipitate was filtered with suction, washed on the filter with boiling water (13 portions of 400 cc. each), and dried at $110^\circ C$. It was subsequently treated in a current of air at $300^\circ C$. for 3 hours. The product weighed about 48 grams; its bulk density, in 2 to 4 mm. granules, was 0.84.

Table 11, rows 12 to 16, contains data on experiments with aluminum oxide-zinc oxide catalysts at 150 and 300 atmospheres pressure and temperatures of 425° and $450^\circ C$. Com-

TABLE 11.—Effect of ZnO on ThO₂, Al₂O₃, and ThO₂-Al₂O₃ catalysts in the isosynthesis

No.	Catalyst				Synthesis conditions						
	Composition, percent			Precipitation procedure ^a	Bulk density, g./cc.	CO:H ₂ in synthesis gas	Pressure, atmospheres	SVH ^b	Temperature, °C.	Conversion, percent	
	ThO ₂	Al ₂ O ₃	ZnO							CO	H ₂
1	0	0	100	I	0.25	41:49	300		450	38	41
2	75	0	25	N	1.19	40:50	300	10	450	70	67
3	75	0	25	N	1.19	40:50	300	3	450	79	79
4	75	0	25	I	1.08	40:50	300	10	450	74	85
5	75	0	25	I	1.08	40:50	300	5	450	74	55
6	75	0	25	I	1.08	48:42	150	10	425	49	61
7	75	0	25	I	1.08	48:42	150	10	450	64	49
8	87	0	13	I		48:42	150	10	450	58	65
9	75	0	25	I	1.09	48:42	300	10	450	77	60
10 ^c	75	0	25	I			300	10	450	73	69
11 ^d	75	0	25	I			300	10	450	77	69
12	0	39	61	I	* 84	49:41	150	10	425	36	73
13	0	39	61	I	* 84	49:41	150	10	450	42	81
14	0	39	61	I	* 84	49:41	150	5	450	54	34
15	0	39	61	I	* 84	41:49	300	10	450	58	46
16 ^f	0	56	44	I		41:49	300	10	450	63	60
17	59	11	30	(*)		51:39	300	10	450	58	61

No.	Yields, g./m ³ (CO:H ₂) gas								i-C ₄ , percent of total C ₄	i-C ₄ H ₁₀ , percent of total i-C ₄
	Hydrocarbon products					Alcohols soluble in—		Total liquids plus gasol		
	C ₁ +	i-C ₄	C ₃ +n-C ₄	C ₂	C ₁	Oil	H ₂ O			
1	0	1.9	1.4	2.0	51	6.9	23.1	33.3	76	74
2	30.7	31.7	14.5	7.7	22.3	5.6	10.1	92.6	87	70
3	37.2	43.2	29.5	20.4	23.4	2.2	2.9	115.0	88	78
4	50.3	26.9	21.8	6.1	10.3	6.0	8.9	113.9	91	82
5	39.7	28.5	31.7	18.0	10.5	7.1	6.8	113.8	87	86
6	58.8	11.6	10.2	1.8	8.4	12.4	4.4	97.4	90	87
7	57.7	16.0	18.0	12.1	21.5	2.5	1.9	96.1	88	81
8	46.2	22.4	21.9	5.6	10.6	4.8	1.6	96.9	89	82
9	78.7	19.3	21.8	4.6	9.9	2.6	5.8	128.2	86	82
10 ^e	67.7	24.0	18.9	7.1	14.0	9.1	3.3	123.0	90	82
11 ^d	45.3	33.5	25.7	13.4	14.0	7.3	4.3	116.1		
12	39.1	3.8	3.8	1.6	3.8	15.0	5.5	67.2	64	84
13	35.5	12.1	14.1	3.7	9.0	4.4	4.1	70.2	68	81
14	41.0	19.5	15.3	3.4	12.3	4.0	4.6	84.4	88	81
15	10.8	26.5	13.9	9.9	26.8	2.5	38.0	91.7	86	81
16 ^f	34.5	24.0	8.5	9.4	19.2	1.1	12.7	80.8	84	81
17	59.2	31.7	20.0	10.0	8.4	6.6	3.3	120.8	87	81

^a I=inverse proportion; N=normal precipitation.

^b SVH=l. outlet gas/28 g. ThO₂ (or 25 cc. catalyst)/hr.

^c This catalyst was prepared as a duplicate of catalyst 9.

^d This catalyst was prepared from more dilute solution than catalysts 9 and 10 (that is, 86 g. Na₂CO₃ was dissolved in 2 liters of water).

^e 2-4 mm. granules.

^f Presence of dimethyl ether was observed in reaction product from this experiment.

* ThO₂ and ZnO were precipitated from the nitrates and Al₂O₃ from the aluminate. Then the three wet precipitates were combined in the desired proportions.

parison of experiments 15 and 16 show that a fairly high aluminum oxide content was necessary to suppress alcohol production. In the test of catalyst 16, which contained 56 Al₂O₃ to 44 ZnO, in parts by weight, the C₃+ hydrocarbon yield was 34.5 grams per cubic meter inert-free feed gas and the i-C₄ hydrocarbon yield was 24.0 grams. Dimethyl ether was present in the reaction products. The yields reported in experiment 16 could be increased somewhat by using a synthesis gas whose carbon monoxide:hydrogen ratio corresponded to the usage ratio. In this way the specific yields, in grams per cubic meter, for aluminum oxide-zinc oxide catalysts would be similar to those obtained with the thorium oxide one-component catalysts (refer to table 8). However, the space-time yields were considerably better from thorium-containing catalysts. Thus, a thorium oxide-aluminum oxide (5:1) catalyst produced

30 grams liquid plus gasol hydrocarbons per liter of catalyst per hour and a conversion of 380 liters CO+H₂ when the space velocity was 600 liters of synthesis gas per liter of catalyst per hour. The catalyst in row 16, table 11 produced 11.6 grams liquid plus gasol hydrocarbons and a conversion of 173 liters CO+H₂ when the space velocity was 340 liters per hour. [From catalysts of equal activity, higher throughput usually produces smaller conversion. However, in the experiments cited, the catalyst containing thorium, which was tested at 600 liters per hour throughput, produced a conversion of 63.4 percent, whereas the thorium-free catalyst tested at a throughput of 340 liters per hour produced a conversion of 51.4 percent.]²²

Comparison of experiments 13 and 14 (150

²² The bracketed sentences have been added by the editor to clarify the thought in the two preceding sentences of the text.