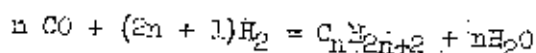


### Effects of the Synthesis Gas Composition

From the general equation for the production of paraffin hydrocarbons from carbon monoxide and hydrogen,



the quantities of carbon monoxide and hydrogen combining chemically in the case of each homologue are as follows:

n	Homologue	Boiling point, °C.	$\frac{2n + 1}{n}$ (usage ratio, H <sub>2</sub> /CO)
1	methane	-164.0	3.00
2	ethane	- 93.0	2.50
3	propene	- 45.0	2.33
4	butane	+ 0.5	2.25
5	pentane	+ 36.0	2.20
6	hexane	+ 69.0	2.17
7	heptane	+ 98.3	2.14

For the production of those paraffins (C<sub>5+</sub>) normally in a liquid state at ordinary temperatures, the H<sub>2</sub>:CO ratio should be maintained below 2.2, as an increase above this value favors the production of gaseous methane, ethane, and propane.

The composition of the synthesis gas may be related to loss of catalyst activity in the following manner: (1) The active centers of the catalyst may be covered by high-boiling hydrocarbons, and (2) carbon may be deposited on the catalyst by the reaction  $2\text{CO} = \text{C} + \text{CO}_2$  and by decomposition of synthesis products. The production of high-boiling hydrocarbons (1) is caused by very rapid polymerization of the free radicals,  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$ , compared to the much slower rate of addition of hydrogen. This tendency may be depressed by using an appropriate excess of hydrogen, the presence of which would also tend to liberate the carbon deposited according to scheme (2). Thus, although too high a concentration of hydrogen is undesirable because it favors the production of gaseous hydrocarbons and reduces the yield of liquid hydrocarbons, it is obvious that from the standpoint of increased catalyst life too low a concentration cannot be tolerated; accordingly, an optimum gas composition must exist. Fischer and Tropsch<sup>20/21</sup> used H<sub>2</sub>:CO water gas at first. However, consideration of the equation for the production of paraffin hydrocarbons from carbon monoxide and hydrogen shows that this composition is not suitable for the production of compounds in the desired molecular-weight range; furthermore, this H<sub>2</sub>:CO ratio decreased the life of the catalyst, and the use of

<sup>20/</sup> Fischer, F., and Tropsch, H., [The Synthesis of Liquid Hydrocarbons]; Brennstoff Chem., vol. 8, No. 1, Jan. 1, 1927, pp. 1-5. (First delivered as a paper before the International Coal Conference, Pittsburgh, Pa., on Nov. 17, 1926.)

<sup>21/</sup> Fischer, F., and Tropsch, H., [Development of the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Ordinary Pressures]; Brennstoff Chem., vol. 11, No. 24, Dec. 15, 1930, pp. 489-500.

$2H_2:1CO$  gas was advocated. Elvins<sup>22/</sup> considered  $1H_2:1CO$  gas as most suitable and stated that a surplus of hydrogen enhanced the production of lighter hydrocarbons and water. Eriley and Nash,<sup>23/</sup> too, found that surplus hydrogen favored the production of lighter hydrocarbons, and that a surplus of carbon monoxide decreased the catalyst life rapidly; thus, Kodama<sup>24/</sup> first used  $1H_2:1CO$  gas, considering it as the most suitable. Kodama and Fujimura,<sup>25/</sup> in an experiment with a Co-Cu-MgO catalyst, used  $1.65H_2:1CO$  gas and found the yield of liquid hydrocarbons was reduced and the production of water was increased. Fujimura and Tsuneoka<sup>26/</sup> found that although surplus carbon monoxide had no ill effect on the synthesis of liquid hydrocarbons, a surplus of hydrogen was extremely harmful in this reaction.

#### Experimental Methods and Results

By using a 100 Co:5 Cu:12  $V_2O_5$ :100 diatomaceous earth catalyst (corresponding to 3 gm. of cobalt), a gas velocity of 6.0 l./hr.,  $H_2:CO$  ratios of 3, 2.5, 2.0, 1.5, and 1 (72.0 l. of synthesis gas for each ratio), by measuring the gasoline ( $C_5+$ ) and water yields and the gas contraction in each case, and by analyzing the last 36.0 l. of the product gases in each experiment, the results shown in table 5 were obtained.

From the gas contraction and from the analyses of the synthesis and product gases, the rates of reaction of carbon monoxide and hydrogen were obtained. The percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons were calculated on the basis of the carbon monoxide in the synthesis gas, and the difference between their sum and 100 was taken as the percentage of carbon monoxide converted into gasoline ( $C_5+$ ). The results are tabulated in table 6.

<sup>22/</sup> Elvins, C. C., Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen: Jour. Soc. Chem. Ind. (Transactions), vol. 46, Dec. 30, 1927, pp. 473-478.

<sup>23/</sup> Work cited in footnote 7.

<sup>24/</sup> Work cited in footnote 10, p. 6.

<sup>25/</sup> Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure, X. The Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 628; supplemental binding pp. 384-386; Sci. Papers Inst. Phys. Chem. Research, vol. 17, Nos. 333-338, pp. 11-21.

<sup>26/</sup> Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XIX. Composition of the Initial Gas Mixture]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1949; supplemental binding pp. 463-467; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 103-112.

TABLE 5. - Effect of synthesis gas composition

(Gas velocity = 6.0 l./hr.; 2.0 l. of synthesis gas used in each case)

Experiment number	Temperature, °C.	H <sub>2</sub> :CO		Synthesis gas composition, percent		Contraction, percent	Liquid products, ml./m. <sup>3</sup> of synthesis gas		Product gas composition, percent						
		H <sub>2</sub>	CO	CO	H <sub>2</sub>		Gasoline (C <sub>5</sub> +) Water		CO <sub>2</sub>	C <sub>m</sub> H <sub>n</sub>	CO	H <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub>		n
							C <sub>5</sub> +	H <sub>2</sub> O					C <sub>n</sub> H <sub>2n+2</sub>	C <sub>n</sub> H <sub>2n+2</sub>	
11A	180	3:1	24.0	75.2	2.8	61.5	107.1	152.4	0.8	4.4	77.4	9.6	1.80	7.6	
11B	190	3:1	24.2	73.2	2.6	67.2	76.2	175.4	1.0	2.3	65.1	23.5	1.12	8.1	
11C	200	3:1	24.0	73.2	2.8	72.0	52.3	191.4	1.8	2	50.5	37.5	1.08	10.0	
12	200	2.5:1	30.2	67.0	2.8	75.2	139.5	185.0	2.0	1	18.2	55.7	1.35	10.8	
13	200	2:1	32.4	64.6	2.8	73.6	143.7	190.3	3.0	1	24.0	49.3	1.58	12.3	
14	200	1.5:1	40.2	57.5	2.3	75.4	137.5	166.6	3.4	2	43.2	40.9	3.7	8.6	
15	200	1:1	48.8	48.2	3.0	64.4	107.1	166.0	3.6	2	58.8	25.4	1.5	10.2	

TABLE 6. - Effect of synthesis gas composition

(Gas velocity = 6.0 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment number	H <sub>2</sub> :CO	CO conversion, percent	H <sub>2</sub> conversion, percent	Carbon distribution							
				Percent of CO in synthesis gas		Percent of CO reacted		Gasoline			
				CO <sub>2</sub>	CO	CO <sub>2</sub>	CO	C <sub>5</sub> +	C <sub>5</sub> +		
11A	3:1	92.9	59.3	1.3	7.1	27.7	63.9	1.4	29.8	31.2	68.8
11B	3:1	96.9	70.8	1.4	3.1	35.7	59.0	1.4	36.8	38.2	61.0
11C	3:1	99.8	80.3	2.1	2	47.3	50.4	2.1	47.3	49.4	50.6
12	2.5:1	85.7	80.2	1.6	14.3	14.0	70.1	1.9	16.8	18.2	81.8
13	2:1	84.1	83.2	2.0	15.9	11.3	70.8	2.4	13.4	15.8	84.2
14	1.5:1	73.6	82.5	2.1	26.4	5.1	66.4	2.2	6.9	9.8	90.2
15	1:1	57.1	81.2	2.6	42.9	3.3	51.2	4.5	5.8	10.4	89.6

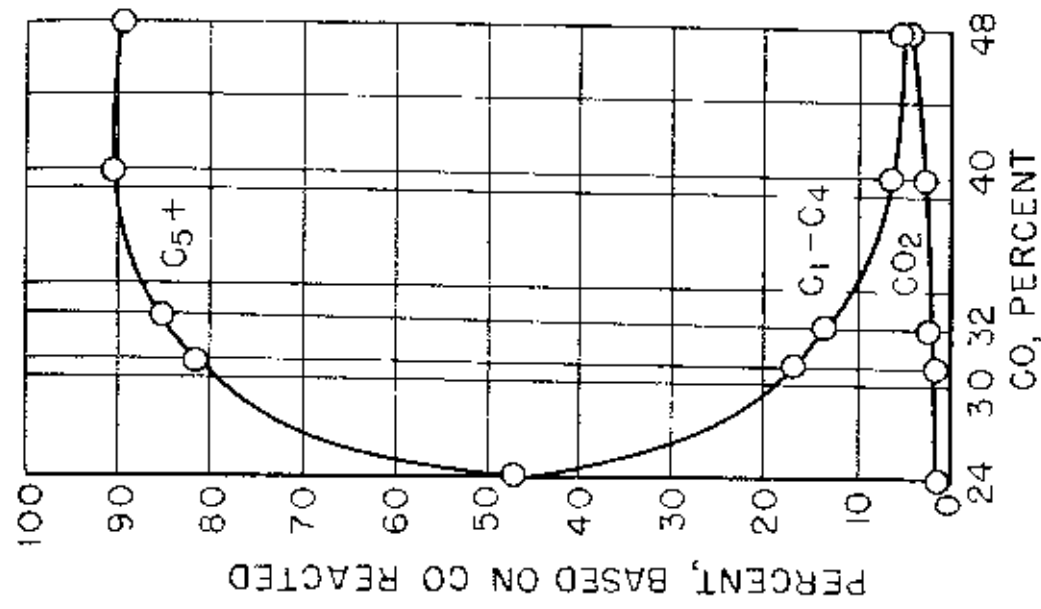


Figure 8.-Effect of synthesis gas composition on hydrocarbon synthesis

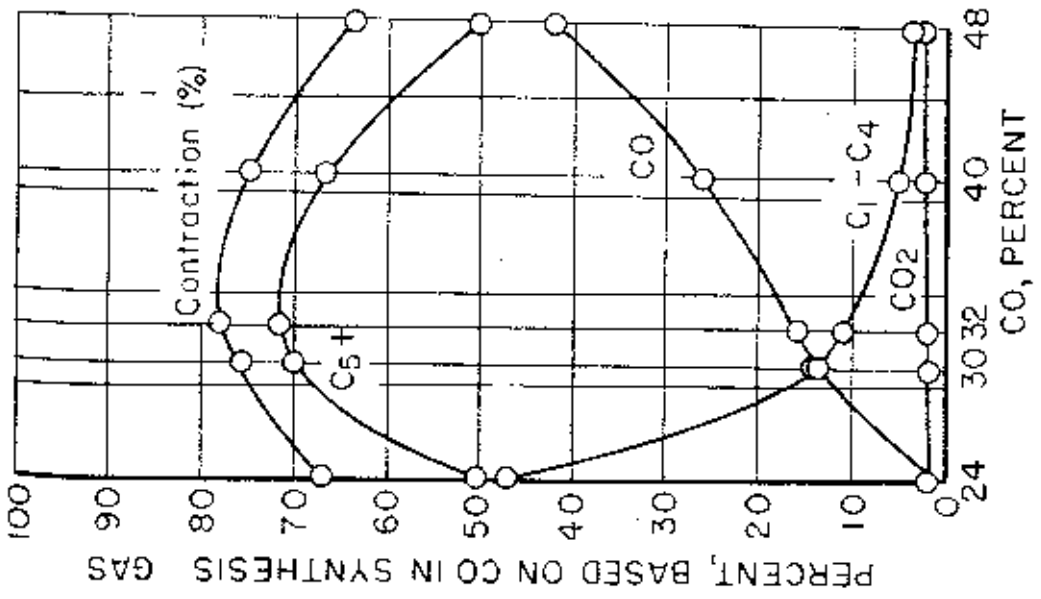


Figure 7.-Effect of synthesis gas composition on hydrocarbon synthesis

The results in table 6 are shown graphically in figures 7 and 8. The experimental results shown in these figures may be summarized as follows:

- (A) The yield of liquid hydrocarbons based on carbon monoxide in the synthesis gas was a maximum (143.7 ml./m.<sup>3</sup>) at an H<sub>2</sub>:CO ratio of 2:1; at an H<sub>2</sub>:CO ratio of 3:1, a satisfactory yield of liquid hydrocarbons was obtained only when the reaction temperature was lowered to 180° C. (B) At an H<sub>2</sub>:CO ratio of 3:1, the carbon monoxide conversion is a maximum, and at 200° C. it is nearly quantitative; the carbon monoxide conversion decreases as the H<sub>2</sub>:CO ratio decreases from this value. In contrast to the behaviour of carbon monoxide, the conversion of hydrogen exhibits a maximum at an H<sub>2</sub>:CO ratio of 2:1, (C) The conversion of carbon monoxide to carbon dioxide increases with decreasing H<sub>2</sub>:CO ratio, whereas the conversion to gaseous paraffins decreases. (D) Based on the carbon monoxide reacted, the conversion of carbon monoxide to carbon dioxide increases with decreasing H<sub>2</sub>:CO ratio; although similar conversion to liquid hydrocarbons also increases with decreasing H<sub>2</sub>:CO ratio, a maximum is exhibited at an H<sub>2</sub>:CO ratio of 1.5:1.

### Discussion

By computing from table 5 the yield of liquid hydrocarbons per cubic meter of carbon monoxide in the synthesis gas, the following results are obtained:

Experiment No.	H <sub>2</sub> :CO	Reaction temperature, °C.	Liquid hydrocarbons	
			ml./m. <sup>3</sup> of CO in synthesis gas	ml./m. <sup>3</sup> of synthesis gas
11A.....	3:1	180	446.2	112
11B.....	3:1	190	314.9	79
11C.....	3:1	200	217.9	54
12.....	2.5:1	200	461.9	132
13.....	2:1	200	443.5	148
14.....	1.5:1	200	342.0	137
15.....	1:1	200	219.5	110

These computations showed a maximum yield of liquid hydrocarbons per cubic meter of carbon monoxide in the synthesis gas at an H<sub>2</sub>:CO ratio of 2.5:1; thus, in order to most effectively utilize carbon monoxide, an excess of two to three times as much hydrogen is necessary. It is also evident from these calculations that at an H<sub>2</sub>:CO ratio of 3:1, lowering the reaction temperature 20° C. below that used at an H<sub>2</sub>:CO ratio of 2:1 yield comparable amounts of liquid hydrocarbons.

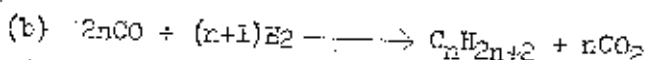
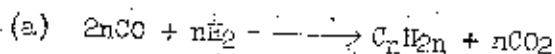
### STUDIES OF CATALYSTS FOR THE HYDROCARBON SYNTHESIS

As catalysts for this reaction, Fischer and Tropsch<sup>27</sup> first used iron compounds. However, iron catalysts produce carbon dioxide during the reaction, complicating utilization of the unreacted gases, and, thus, nickel or cobalt catalysts have been used more recently. According to Fischer and Koch,<sup>28</sup> the general equations for these catalytic reactions are:

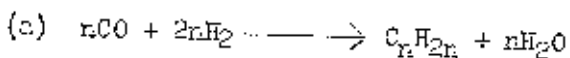
<sup>27</sup> Work cited in footnote 6.

<sup>28</sup> Fischer, F., and Koch, H., [The Chemistry of the Hydrocarbon Synthesis and General Properties of the Resulting Products (Gasol, Gasoline, Diesel Oil, and Paraffin Waxes)]: Brunnstoff Chem., vol. 13, No. 22, Nov. 15, 1932, pp. 428-434.

In the case of iron catalysts;



In the case of nickel or cobalt catalysts;



In other words, with iron catalysts the reaction is characterized by the production of carbon dioxide, whereas, with nickel or cobalt catalysts water is produced. Oxygen liberated when the carbon monoxide combines with iron, nickel, or cobalt (to produce their respective carbides) reacts with other carbon monoxide, in the case of iron catalyst, to produce carbon dioxide, and with hydrogen, in the case of nickel or cobalt catalyst, to produce water. Because of the inexpensiveness of iron catalysts as compared with nickel or cobalt catalysts, the development of an iron catalyst with an activity as high as that of nickel or cobalt catalysts would be highly desirable industrially. This problem will be treated in a later report; investigations involving nickel, cobalt, or nickel-cobalt mixed catalysts are reported here.

A synthesis of this type, as explained previously, is most advantageously carried out at low reaction temperatures. Hence, it is necessary that a catalyst of the greatest possible activity be utilized in order to operate in the desired low-temperature range. It is a generally accepted fact that catalysts that are prepared by precipitation have a much higher activity than those obtained by calcination of mixed salts of the catalyst components. Thus, Fischer and Meyer<sup>29</sup> and Fischer and Koch<sup>30</sup> used a catalyst that was obtained by precipitation with alkali from mixed nitrate salt solution and succeeded in lowering the reaction temperature to approximately 200° C. The activity of a precipitated catalyst, however, is greatly affected by the type of precipitant, the method of precipitation, and the method of removing electrolytes. For example, when such precipitants as ammonia and ammonium carbonate are used, there is no electrolyte-removal problem; when alkali is used, quantitative removal of the adsorbed precipitant is virtually impossible, no matter how carefully the precipitate is washed. The minute quantities of precipitant thus remaining may have a material effect upon the activity of the catalyst; accordingly, the selection of precipitant is vital. Fischer established alkaline carbonates as the best precipitants for nickel or cobalt catalysts, considering it most effective to have a quantity of alkaline carbonate remain after washing the precipitate with a constant amount of water. This method of controlling the amount of alkaline carbonate in the catalyst is subject to considerable difficulty; a more satisfactory method is to add a constant quantity of alkaline carbonate to the precipitate after it has been thoroughly water washed, as done by Fujimura and Tsuneko.<sup>31</sup>

<sup>29</sup>/ Work cited in footnote 12.

<sup>30</sup>/ Work cited in footnote 13.

<sup>31</sup>/ Fujimura, K., and Tsuneko, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XIII and XIV. Nickel Catalysts]; Jour. Soc. Chem. Ind. Japan, vol. 36, 1953, p. 379; supplemental binding pp. 119-121; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1953, pp. 242-253.

## Effects of the Carrier

It has been widely acknowledged that the effectiveness of hydrogenation catalysts, such as nickel, cobalt, and iron, is remarkably promoted by the use of inorganic carriers, such as diatomaceous earth, pumice, and asbestos. Of great significance from economic considerations is the fact that in the hydrocarbon synthesis the presence of a suitable carrier enhances both the reaction rate and the yield of liquid hydrocarbons. Fischer<sup>32/</sup> considered the "stüttgarter masse" (artificial stone made of granular quartz and water glass) the most suitable carrier for Co-Cu catalysts. For Co-Cu-MgO catalysts, Fujimura<sup>33/</sup> used 200-mesh powdered or 3-mm. granular pumice as a carrier and added cane sugar along with the nitrate salts during the preparation of the catalyst; the calcined catalyst produced an increased yield of liquid hydrocarbons.

Fischer and Meyer<sup>34/</sup> and Fischer and Koch<sup>35/</sup> found diatomaceous earth superior as a carrier for precipitated nickel or cobalt catalysts. These workers considered a low bulk density as highly desirable in a carrier and utilized an air-separated material from one locality with a bulk density of about 0.1. A comparison of this material with Merck diatomaceous earth having a bulk density of 0.0337 shows the yield of liquid hydrocarbons in the latter case was only one-fifth of the former. Magnesia was found to be unsuitable as a carrier. The most suitable ratio between metal and diatomaceous earth was determined as 1:1 for nickel catalysts and 1:1.5 for cobalt catalysts. Fujimura<sup>36/</sup> used 10 to 12 gm. of diatomaceous earth per 3 gm. of cobalt as a carrier for cobalt-copper catalysts and added starch along with the nitrate salts; an increased yield of liquid hydrocarbons was obtained. Fischer and Meyer<sup>37/</sup> used silica or graphite with good heat-conducting properties rather than diatomaceous earth; calcium carbonate, or basic magnesium carbonate in Ni-Mn-Al<sub>2</sub>O<sub>3</sub> catalysts but did not obtain satisfactory results.

### Amount of Carrier

By using a 100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub> catalyst corresponding to 3 gm. of cobalt and by varying the cobalt:diatomaceous earth ratio utilizing 72.0 l. of synthesis gas in each case, the results listed in table 7 were obtained.

<sup>32/</sup> Work cited in footnote 21.

<sup>33/</sup> Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure IX. Additional Tests with a Cobalt-Copper-Magnesium Oxide Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 1005; supplemental binding No. 7, pp. 227-229.

<sup>34/</sup> Work cited in footnote 12.

<sup>35/</sup> Work cited in footnote 3.

<sup>36/</sup> Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XI. Cobalt-Copper-Thorium and Cobalt-Copper-Uranium Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 35, 1932, p. 532; supplemental binding pp. 179-182; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 189-197.

<sup>37/</sup> Fischer, F., and Meyer, K., [Effect of Preparation Conditions on the Activity of Nickel-Manganese-Aluminum Catalysts]: Brennstoff Chem., vol. 14, No. 3, Feb. 1, 1933, pp. 47-50.

TABLE 7. - Effect of carrier

(Gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment number	Cobalt-kieselguhr ratio	Temperature, °C.	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./m. <sup>3</sup> of synthesis gas		Product gas composition, percent						
			CO	H <sub>2</sub>	N <sub>2</sub>		Gasoline (C <sub>5</sub> +)	Water	CO <sub>2</sub>	C <sub>m</sub> H <sub>n</sub>	CO	H <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub>	n	N <sub>2</sub>
16.....	3:1	200	32.8	65.0	2.2	78.8	122.7	190.4	7.8	0.2	19.8	46.2	16.9	1.36	9.1
17.....	2:1	200	32.2	65.6	2.2	80.4	120.8	200.0	7.2	.1	24.7	40.1	16.2	1.37	11.7
18A.....	1:1	190	32.5	64.8	2.7	75.4	133.3	179.2	2.0	-	20.0	57.7	10.3	1.53	10.0
18B.....	1:1	200	32.8	65.0	2.2	80.6	143.3	193.7	4.6	.2	23.4	43.8	16.5	1.31	11.5
19A.....	3:4	190	32.8	64.9	2.3	78.5	143.0	198.5	2.0	.1	24.0	52.2	11.8	1.52	9.9
19B.....	3:4	200	32.5	65.0	2.5	80.6	140.5	206.6	4.4	-	25.4	44.5	12.8	1.31	12.9



In the usual manner, the carbon monoxide and hydrogen conversions were obtained from a knowledge of the gas contraction and the analyses of the synthesis and product gases; the percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons were then calculated on the basis of the carbon monoxide in the synthesis gas, and their sum was subtracted from 100, the difference being the percentage of carbon monoxide converted into gasoline ( $C_{5+}$ ). These results are given in table 8. From these tables it is evident that as the diatomaceous earth content of the catalyst is increased, the yield of gasoline also is increased and passes through a maximum at a metal:carrier ratio of 1:1 or 3:4. However, table 8 shows that the carbon monoxide conversion was about the same at all ratios, and that the increase or decrease in the yield of gasoline ( $C_{5+}$ ) was governed by the quantities of carbon dioxide and gaseous saturated hydrocarbons produced. As the production of carbon dioxide and gaseous saturated hydrocarbons is accelerated with increase in temperature at high metal:carrier ratios, the temperature of the catalyst itself may be considered to be increased. That is, at a cobalt:diatomaceous earth ratio of 3:1, if reaction starts at a given point the heat of reaction can easily be transmitted through a small quantity of diatomaceous earth and activate the adjacent active center. In this manner, the heat of reaction is propagated throughout the catalyst mass, and the reaction takes place at a large number of the active centers. Hence, the temperature of the catalyst is raised by the heat of the reaction, and the production of carbon dioxide and gaseous saturated hydrocarbons is accelerated. At cobalt:diatomaceous earth ratios of 3:4 or 1:1, the heat of reaction generated at a given active center is transmitted to the diatomaceous earth, but, as the quantity of diatomaceous earth is large, less energy is received by the adjacent active center, and the resulting activation is correspondingly smaller. Therefore, the production of carbon dioxide and gaseous saturated hydrocarbons is likewise smaller.

On the basis of these considerations, it is postulated that in this reaction the number of active centers at cobalt:diatomaceous earth ratios of 3:4 or 1:1 is sufficient for the synthesis, and at ratios of 3:1 or 2:1 there are more than the necessary number of active centers.

#### Type of Carrier

The effect of carriers other than diatomaceous earth is shown in table 9. A weight ratio of 1:1 of cobalt to pumice, kaolin, or silica gel was used. The catalyst sample contained 3 gm. of cobalt in a composition of 100 Co:5 Cu:12  $U_3O_8$ .

Experiment 20. - Unrefined commercial kaolin was used, and the production of carbon dioxide and gaseous saturated hydrocarbons was much larger than that of experiment 18, in which diatomaceous earth was used.

Experiment 21. - Granular pumice was pulverized to 120-mesh. It was then boiled for several hours with concentrated nitric acid to remove the iron particles. After thorough water washing and drying at about 120° C., the pumice was ready to use. The volume of carbon dioxide and gaseous saturated hydrocarbons in the product gas was generally similar to that obtained when kaolin was used.

TABLE 8. - Effect of carrier

Experiment No.	CO conversion, percent	H <sub>2</sub> conversion, percent	Carbon distribution							
			Percent of CO in synthesis gas			Percent of CO reacted				
			CO <sub>2</sub>	CO	C <sub>n</sub> H <sub>2n+2</sub> (C1-C <sub>n</sub> )	Gasoline (C <sub>5</sub> +)	CO <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub> (C <sub>1</sub> -C <sub>n</sub> )	CO <sub>2</sub> +C <sub>n</sub> H <sub>2n+2</sub>	
16.....	67.3	84.9	5.0	12.7	14.8	67.5	9.7	17.0	22.7	77.3
17.....	85.0	88.0	4.4	15.0	13.5	67.1	5.2	15.9	21.1	78.9
18A.....	84.2	78.1	1.5	15.1	11.9	71.5	1.8	14.0	15.8	84.2
18B.....	86.2	86.9	2.7	13.8	12.8	70.7	3.1	14.0	17.9	82.1
19A.....	84.3	82.7	1.3	15.7	11.8	71.2	1.5	14.0	15.5	84.5
19B.....	84.8	86.7	2.6	15.2	10.1	72.1	3.1	11.9	15.0	85.0

TABLE 9. - Effect of carrier

(Catalyst = 100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub>; gas velocity = 6 l./hr.; 72.0 l. synthesis gas used in each case.)

Experiment No.	Carrier	Reaction temperature, °C.	Composition of synthesis gas, percent			Contraction, percent	Liquid products, ml./m.3 of synthesis gas			Product gas composition, percent					
			CO	H <sub>2</sub>			Gasoline (C <sub>5</sub> +)	Water	CO <sub>2</sub>	C <sub>n</sub> H <sub>n</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>n</sub> H <sub>2n+2</sub>	n	N <sub>2</sub>
				CO	H <sub>2</sub>										
20.....	Kaolin	200	31.6	65.0	3.4	78.0	112.5	187.9	9.6	0.4	12.2	40.1	22.2	1.64	15.5
21.....	Pumice	200	33.0	64.2	2.8	76.8	116.6	195.8	7.8	1.2	14.0	43.8	22.9	1.20	11.3
22.....	Silica gel	210	32.8	64.0	3.2	76.3	125.0	175.0	4.6	-	19.0	54.0	9.0	1.30	13.4

Experiment 22. - Unrefined silica gel was used, which was salt-free and very voluminous and which had been obtained from Dr. Altpeter and Dr. Richter, Czechoslovak Laboratories. At 200° C., unfavorable yields of liquid hydrocarbons and poor gas contractions were obtained, and it was necessary to raise the temperature to 210° C. This catalyst was the least active of the three tested in this group.

From tables 7 and 9, it is evident that the yield of gasoline (C<sub>5+</sub>) is considerably smaller when kaolin, pumice, or silica gel was the carrier than when diatomaceous earth was used. Correspondingly, large amounts of carbon dioxide and gaseous saturated hydrocarbons were produced when pumice and kaolin were used. In view of the results obtained with diatomaceous earth, which suggested that decreasing amounts of carrier produced increasing catalyst temperatures (as indicated by the increased production of carbon dioxide and gaseous saturated hydrocarbons), the necessity of raising the operating temperature to obtain a significant yield of liquid hydrocarbons in the silica-gel experiment may be attributed to the presence of an excessive quantity of carrier. As the bulk densities of pumice and kaolin are four times greater than that of diatomaceous earth, weights of these materials four times that of diatomaceous earth would have to be used to obtain an equivalent volume of carrier in each case. Conversely, the bulk density of silica gel is half that of diatomaceous earth, and a weight of silica gel equal to only half the weight of the diatomaceous earth would be needed. These relationships are shown in the following table 10.

TABLE 10. - Relationship of carrier bulk densities

Carrier	Volume of 3 gm. of carrier, ml.	Weight of carrier equivalent in volume to 3 gm. of diatomaceous earth	Bulk density gm./ml.
Diatomaceous earth.....	17	3	0.18
Pumice.....	4	13	.75
Kaolin.....	4	13	.75
Silica gel.....	34	1.5	.09

Studies of the effects of the carrier were then undertaken on the basis of a constant volume rather than a constant weight. Experimental results obtained by incorporating in the catalyst (100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub>, weight of cobalt = 3 gm.) quantities of pumice, kaolin, and silica gel, respectively, corresponding to 17 ml. of diatomaceous earth are shown in table 11.

Experiment 23. - Using Kaolin at 200° C., neither favorable gas contraction nor gasoline (C<sub>5+</sub>) yield was indicated, and it was necessary to raise the temperature to 210° C. On comparing this experiment with experiment 20, it is evident that the volumes of carbon dioxide and gaseous saturated hydrocarbons in the product gases were reduced, but because the gas contraction was reduced at the same time, the yields of gasoline were approximately the same in both experiments. In experiment 23, extremely rapid deterioration in catalyst activity was observed.

TABLE II. - Effects of the carrier

(100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub> catalyst; reaction temperature = 210° C.; gas velocity = 5 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Carrier	Weight, gm.	Composition of synthesis gas, percent.			Contraction, Percent	Liquid products, ml./m. <sup>3</sup> of synthesis gas		Product gas composition, percent							
			CO		H <sub>2</sub>		N <sub>2</sub>	Gasoline (C <sub>5</sub> +)	Water	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub> +2	n	H <sub>2</sub>
			33.0	63.8												
23	Kaolin	13	33.0	63.8	3.2	70.5	114.2	178.0	2.0	0.2	29.0	57.5	5.2	1.32	5.1	
24	Pumice	13	33.8	64.0	2.2	73.2	115.6	175.0	3.0	.4	28.2	54.0	7.2	1.40	7.2	
25	Silica gel	1.5	32.8	64.8	2.4	77.6	128.2	193.7	6.0	-	26.4	45.0	13.4	1.22	9.2	

Experiment 24. - In this experiment, in which pumice was used, it was necessary, as in experiment 23, to increase the temperature to 210° C., and the yield of gasoline (C<sub>5+</sub>) was not greatly different here from that of experiment 21, in which 3 gm. of pumice was used. Signs of low catalyst durability also were observed.

Experiment 25. - Although half the weight of silica gel previously used was employed in this experiment, the reaction temperature could not be lowered; 210° C. was still the most suitable operating temperature. The gas contraction was somewhat greater here, but, as the production of carbon dioxide and gaseous saturated hydrocarbons also was increased, only a very small increase resulted in the yield of gasoline. In this experiment, however, the durability of the catalyst was found to be high, as in the case of diatomaceous earth.

These results indicate that kaolin, pumice, and silica gel are inferior to diatomaceous earth as carriers. With respect to bulk density, it is believed that the larger the bulk volume per unit weight, the better the results. However, although the bulk density of silica gel is one half that of diatomaceous earth, its function as a carrier is inferior to diatomaceous earth. The explanation for this apparently contradictory behaviour may lie in the role the carrier may play as a simple carrier as well as the part played by its binding properties. As the bulk densities of kaolin and pumice were equal, and as similar results were obtained in each case, no violent poisoning action can be attributed to the alumina in the kaolin as described by Fischer and Koch.<sup>38/</sup>

#### Effects of Raw Materials Used in Catalyst Preparation

The effects of the raw materials used in preparing the catalyst were determined by preparing 100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub> catalyst from cobalt sulfate, cobalt chloride, cobalt nitrate, and cobalt acetate solutions. The activities of the resulting catalysts are compared in table 12. The salt solutions were prepared as described in the Experimental section, and the precipitates were obtained by the addition of potassium carbonate solution. The precipitates then were thoroughly water-washed to minimize the remaining sulfate, chloride, nitrate, and acetate salts. The results obtained for cobalt nitrates in experiments 18A and B are listed again for convenience in comparison.

Experiments 26A and B. - In this experiment, cobalt sulfate (Kato, guaranteed) was used. The catalyst was first reduced in hydrogen at 250° C. for 1 hour. Then the flow of synthesis gas was started, and, at 210° C., 60.4 ml. of gasoline (C<sub>5+</sub>) was obtained per cubic meter of synthesis gas. This yield increased to 81.2 ml./m.<sup>3</sup> at 220° C., an activity considerably less than that exhibited in experiment 18A, in which nitrate salts were used. The cause for this decreased activity may be linked with the potassium sulfate produced by the reaction between cobalt sulfate and potassium carbonate. If the potassium sulfate is not adequately removed by water washing, the remainder may be absorbed into the precipitate and exert a subsequent poisoning effect on the catalyst. As residual potassium nitrate seems to exert no poisoning effect, the poisoning action of potassium sulfate may be presumed to be due to the action of negative SO<sub>4</sub><sup>=</sup> ions.

<sup>38/</sup> Work cited in footnote 3.

TABLE 12. - Effects of raw materials from which catalyst is prepared

(100 Co:5 Cu:12  $U_3O_8$  catalyst equivalent to 3 gm. of Co;  
gas velocity = 6 l./hr.)

Experiment No.	Raw material	Reaction temperature, °C.	Amount of gas used, liters	Gas contraction, percent	Liquid products, ml./r. <sup>3</sup>	
					Gasoline (C <sub>5+</sub> )	Water
26A.....	Sulfate	210	56.0	48.5	60.4	83.3
26B.....	Sulfate	220	56.0	53.4	81.2	108.3
27.....	Chloride	210	36.0	0	0	0
18A.....	Nitrate	190	72.0	75.4	133.3	179.2
18F.....	Nitrate	200	72.0	80.6	143.3	193.7
26A.....	Acetate	190	72.0	76.3	130.5	185.0
26B.....	Acetate	200	72.0	81.5	145.2	200.0

Experiment 27. - In this experiment, cobalt chloride (Kato, guaranteed) was used. In spite of reduction in hydrogen for 1 hour at 250° C., no signs of activity were found at operating temperatures up to 220° C. A violent poisoning effect on this catalyst is thus exhibited by Cl<sup>-</sup>.

Experiment 26A and F. - In this experiment, cobalt acetate (Kato, pure) was used. After hydrogen reduction at 200° C. for 1 hour, the flow of synthesis gas was started. At 190° and 200° C., 130.5 ml. and 145.2 ml. of gasoline (C<sub>5+</sub>), respectively, were produced per cubic meter of synthesis gas; this activity is virtually the same as that obtained in catalysts prepared from nitrate salts. As CH<sub>3</sub>COO<sup>-</sup> exerts no poisoning effect on the final catalyst, cobalt acetate, like cobalt nitrate, may be used effectively as a raw material in catalyst preparation.

#### Nickel Catalyst

The production of methane by hydrogenation of carbon monoxide over reduced nickel was first investigated by Sabatier and Senderens<sup>39/</sup> in 1902. According to these investigators, the hydrogenation of carbon monoxide commences at 180° to 200° C. when reduced nickel is used, and a steady production of methane is obtained at 230° to 250° C. Orlov<sup>40/</sup> reduced carbon monoxide over asbestos impregnated with nickel and palladium and found that unsaturated compounds were produced at a comparatively low temperature (100° C.). Medsforth,<sup>41/</sup> in his investigation of the production of methane, added various difficulty reducible metal oxides to reduced nickel on the theory that as the reduction of carbon monoxide to methane entailed a dehydrating reaction it was desirable to use these oxides, which are known to be dehydrating catalysts. Metallic oxides were found to be decreasingly effective in promoting this reaction, in the following order: CoO<sub>2</sub>, ThO<sub>2</sub>, CoO, Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and ZrO<sub>2</sub>. Russell and

<sup>39/</sup> Sabatier, P., and Senderens: Compt. rend., vol. 134, 1902, p. 514.

<sup>40/</sup> Orlov, G., Jour. Russian Phys. Chem., vol. 40, 1909, p. 1588.

<sup>41/</sup> Medsforth, S., Promotion of Catalytic Reactions I: Jour. Chem. Soc., vol. 123, 1923, pp. 1452-1469.

Taylor<sup>42/</sup> studied the absorption action of reduced nickel in the reaction  $\text{CO}_2 + 4\text{H}_2 \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ , and found that when a small quantity of thoria was added to the reduced nickel the over-all reaction rate was increased 10 times, but the increase in the absorption rate was only several tenths of a percent. They inferred from this that absorption and catalytic activity were not directly related. Fischer and Tropsch<sup>43/</sup> and Elvina<sup>44/</sup> predicted that, as nickel had excellent hydrogenation properties, methane would be produced with ease, but that the production of high-boiling liquid hydrocarbons would be difficult. However, Fischer and Meyer<sup>45/</sup> succeeded in preparing a highly practical nickel catalyst for gasoline ( $\text{C}_{8+}$ ) production and have increased this yield remarkably by lowering the reaction temperature to about 200° C.

In this country, Fujimura and Tsuneoka<sup>46/</sup> of Kyoto Imperial University studied nickel catalysts. They observed the effect of adding alkali carbonates to nickel-manganese and nickel-thoria catalysts and of adding various promoters to nickel-manganese catalysts.

### Experimental Procedure

Catalyst. - To a nickel nitrate solution corresponding to 3 gm. of nickel was added a solution containing a fixed percentage (with regard to nickel) of nitrates of manganese, cerium, alumina, or thoria. An appropriate amount of diatomaceous earth was then added, followed by an amount of potassium carbonate slightly in excess of the stoichiometric equivalent. The precipitate was filtered and dried on a water bath. It was then spread in a layer in the 2½-centimeter-long constant-temperature zone of the reaction tube and reduced in hydrogen for 4 to 5 hours at a temperature of 350° to 450° C. When uranium oxide, tungsten oxide, or silica gel was used as a promoter, nickel and manganese carbonates were precipitated on the diatomaceous earth. Uranium oxide was then added by precipitating the nitrate with ammonia; tungsten oxide was added as the oxide obtained by dissolving the ammonium salt with concentrated nitric acid; and the silica gel was added after having been boiled with distilled water for 2 to 3 hours and dried at about 120° C.

Synthesis gas. -  $\text{CO}:\text{H}_2 = 1:2$  was used.

### Results

(A) Nickel-manganese catalysts. - Fischer and Meyer<sup>47/</sup> considered a manganese content of 15 to 20 percent that of nickel as most suitable while Fujimura and Tsuneoka<sup>48/</sup> considered 15 percent the optimum. These variations in results

<sup>42/</sup> Russell, W. W., and Taylor, R. S., The Promoter Action of Thoria on Nickel Catalysts: Jour. Phys. Chem., vol. 29, 1925, pp. 1325-1341.

<sup>43/</sup> Work cited in footnote 6.

<sup>44/</sup> Work cited in footnote 22.

<sup>45/</sup> Work cited in footnote 12.

<sup>46/</sup> Work cited in footnote 31.

<sup>47/</sup> Work cited in footnote 12.

<sup>48/</sup> Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XV and XVI. Nickel Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 36, 1933, p. 999; supplemental binding pp. 413-415; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 254-263.

may be attributed to differences in manufacturing conditions and carrier properties. Results obtained at manganese contents of 12, 16, and 20 percent, respectively, are shown in table 13.

TABLE 13. - Nickel-manganese catalysts; effect of manganese content  
(3 gm. of Ni + 3 gm. of diatomaceous earth; gas velocity = 6 l./hr.)

Experiment No.	Composition of catalyst	Reaction temperature, °C.	Volume gas used, liters	Gas contraction, percent	Liquid products ml./m. <sup>3</sup>	
					Gasoline (C <sub>5+</sub> )	Water
29.....	Ni + 12% Mn	205	72.0	58.0	65.3	135.6
30.....	Ni + 16% Mn	205	72.3	70.5	100.0	152.8
31A.....	Ni + 20% Mn	200	36.0	68.5	92.3	148.5
31B.....	Ni + 20% Mn	205	72.0	72.5	107.6	160.6

A manganese content of 20 percent was found to be the optimum, producing a yield of liquid hydrocarbons, equal to 107.6 ml./m.<sup>3</sup> of synthesis gas. When hydrogen peroxide was added to a solution of nickel and manganese nitrates, and manganese dioxide was precipitated to produce a catalyst containing 20 percent manganese, no change was obtained in the liquid hydrocarbon yield. A reaction temperature of 205° C. produced a better gasoline yield than a temperature of 200° C. although an increase in the reaction temperature is usually associated with an increased production of gaseous saturated hydrocarbons and a reduction in the yield of liquid hydrocarbons. The results obtained on reducing the quantity of diatomaceous earth from 3 gm. of 2.5, 2, and 1.5 gm. in an attempt to lower the reaction temperature are shown in table 14.

TABLE 14. - Nickel-manganese catalysts; effect of carrier content

(3.0 gm. Ni + 0.6 gm. Mn; gas velocity = 6 l./hr.;  
72.0 l. of synthesis gas used in each case)

Experiment No.	Diatomaceous earth, gm.	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>	
				Gasoline (C <sub>5+</sub> )	Water
32.....	2.5	200	73.4	114.0	160.0
32A.....	2.0	200	75.0	120.5	170.6
32B.....	2.0	205	75.8	108.0	175.0
34.....	1.5	200	73.0	118.0	170.5

Although a slight increase in gas contraction was observed with smaller quantities of diatomaceous earth, no material difference was evident in the activities of the three catalysts. The largest yield of gasoline (C<sub>5+</sub>) was obtained at a carrier content of 2.0 gm., and a temperature of 200° C. was found to be more favorable than 205° C.

The effects of adding 4 percent (based on nickel) of uranium oxide, cerium oxide, alumina, or tungsten oxide to a catalyst containing Ni + 20 percent Mn + 66 percent diatomaceous earth are shown in table 15.



TABLE 15. - Nickel-manganese catalysts; effect of promoters

(100 Ni:20 Mn:4 promoter:66 diatomaceous earth; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Promoter	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>	
				Gasoline (C <sub>5+</sub> )	Water
35.....	U <sub>3</sub> O <sub>8</sub>	190	78.4	138.5	185.2
36.....	CoCO <sub>2</sub>	200	72.5	125.0	178.5
37.....	Al <sub>2</sub> O <sub>3</sub>	200	74.2	132.6	180.5
38.....	WO <sub>3</sub>	200	71.8	128.0	183.0

Experiment No. 35. - Fujimura and Tsuneoka<sup>49/</sup> had found previously that uranium oxide was effective as a promoter for nickel. In the catalysts in the present experiments, nickel and manganese were precipitated as carbonates by potassium carbonate, and to this was added ammonium uranumate, obtained by adding ammonia to uranium nitrate. The catalyst thus prepared showed a considerably greater activity than Ni + 20 percent Mn, for the reaction temperature, 190° C., was 10° lower.

Experiment No. 36. - Cerium oxide was used by Eriley and Wash<sup>50/</sup> and Kodama<sup>51/</sup> as a promoter for cobalt-copper catalysts, but it had never been tried on nickel. Accordingly, such a catalyst was prepared by precipitating the cerium along with nickel and manganese as the carbonates by potassium carbonate. Only a slight increase in activity was exhibited; however, over that of Ni + 20 percent Mn catalyst. Cerium oxide is not an effective promoter, therefore, for this type of catalyst.

Experiment No. 37. - Fischer and Meyon<sup>52/</sup> and Fujimura and Tsuneoka<sup>53/</sup> reported that alumina was a superior promoter for nickel-manganese catalysts. Therefore, nickel and manganese were precipitated as the carbonate salts by potassium carbonate, and a definite amount of alumina was added by treating an aluminum nitrate solution with ammonia. The resulting preparation showed a superior gas contraction and gasoline (C<sub>5+</sub>) yield.

Experiment No. 38. - A catalyst was prepared by adding tungsten oxide, obtained by dissolving ammonium tungstate in concentrated nitric acid, to mixed carbonate salts of nickel and manganese. The promoting action of tungsten oxide was similar to that of cerium oxide, for the resulting activity was low.

Various combinations of the effective promoters, uranium oxide and alumina, were next tried with the results shown in table 16.

<sup>49/</sup> Work cited in footnote 31.

<sup>50/</sup> Work cited in footnote 7.

<sup>51/</sup> Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure V. The Influence of Titanium Oxide, Zirconium Oxide, and Cerium Oxide]; Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 620; supplemental binding (in German), pp. 202-203; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, Nos. 257-259, 1930, pp. 13-25.

<sup>52/</sup> Work cited in footnote 12.

<sup>53/</sup> Work cited in footnote 48.

TABLE 16. - Nickel-manganese catalysts; effect of promoters

(Ni + 20% Mn catalyst equivalent to 4 gm. of nickel; reaction temperature = 200° C.; gas velocity = 6 l./hr.)

Experiment No.	Promoter percent	Volume gas used, l.	Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>	
				Gasoline (C <sub>5</sub> +)	Water
39A/.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	84.8	152.0	218.5
39B1.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	85.0	150.5	216.0
39B2.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	88.2	159.0	218.5
39B3.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	86.6	158.2	210.0
39B4.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	86.2	154.0	208.2
39B5.....	8 U <sub>3</sub> O <sub>8</sub>	72.0	86.5	154.2	208.0
39C.....	8 U <sub>3</sub> O <sub>8</sub>	360.0	85.5	155.2	212.1
40a/.....	8 Al <sub>2</sub> O <sub>3</sub>	72.0	73.2	118.6	169.0
41.....	8 U <sub>3</sub> O <sub>8</sub>	216.0	84.8	166.5	220.0
42.....	4 Al <sub>2</sub> O <sub>3</sub>	216.0	84.2	162.3	218.5
	4 WO <sub>3</sub>				
43.....	8 U <sub>3</sub> O <sub>8</sub>	216.0	87.8	168.8	226.0
	4 ThO <sub>2</sub>				
44.....	10 Silica gel	72.0	74.5	122.6	175.0

a/ Catalyst equivalent to 3 gm. of nickel used.

Experiment Nos. 39A, B, and C. - Ni + 20 percent Mn + 8 percent U<sub>3</sub>O<sub>8</sub> catalyst corresponding to 3 gm. of nickel was used in experiment 39A. The nickel content was then increased from 3 to 4 gm. to test the durability of the catalyst. Five tests, designated as experiment 39B-1, 2, 3, 4, and 5, were made with 72.0 l. of synthesis gas for each. In the first test the yield of gasoline (150.5 ml./m.<sup>3</sup>) was comparatively low, considering the large gas contraction, a result of the large production of gaseous hydrocarbons. The production of gasoline then increased to 159.0 ml. per cubic meter of synthesis gas in the second test and decreased in the remaining tests, resulting in an average value for the 360.0 l. of synthesis gas of 155.2 ml./m.<sup>3</sup> (experiment 39C).

Upon completion of each separate experiment, the synthesis gas in the reaction tube was displaced by hydrogen; therefore, the carbon and the high-boiling hydrocarbons deposited on the catalyst, which may cause the catalyst to deteriorate, may have reacted to some extent with the hydrogen and in this manner may have been removed from the reaction tube. Hence, it is possible that the catalyst may have been partly reactivated. Because hydrogen is known to diffuse through rubber tubing, and because of the contraction of the cooled gases, the internal pressure was decreased, and it is probable that a small amount of air was taken into the system. Consequently, possible oxidation from this source must also be considered. Operation on a continuous basis over a prolonged period to study the true durability of the catalyst will be discussed elsewhere.

Experiment No. 40. - Increasing the alumina content from 4 to 8 percent reduced the activity considerably; 118.6 ml. of gasoline was obtained, compared to the previous yield of 132.6 ml./m.<sup>3</sup> of synthesis gas.

Experiment Nos. 41 to 43. - Eight percent uranium oxide has been shown to be the best promoter for Ni + 20 percent Mn catalyst. In an attempt to activate the catalyst composition still further, 4 percent of alumina, tungsten oxide, or thoria was added to Ni + 20 percent Mn + 8 percent U<sub>3</sub>O<sub>8</sub> catalyst (corresponding to 4 gm. of nickel). These materials proved decreasingly effective in the order: thoria, alumina, and tungsten oxide, producing 168.3, 166.5, and 162.3 ml. of gasoline per cubic meter of synthesis gas, respectively.

Experiment No. 44. - According to Brückner and Jacobus,<sup>54/</sup> if 10 percent silica gel is added to nickel, the production of methane by catalytic hydrogenation of carbon monoxide is increased about 2.5 times, and the durability of the catalyst is increased significantly. However, in this experiment, when silica gel corresponding to 10 percent of nickel was added to Ni + 20 percent Mn catalyst, activity was increased only slightly.

(B) Nickel-uranium oxide catalysts. - Fujimura and Tsunocka<sup>55/</sup> showed that uranium oxide was effective as a promoter for nickel; these workers used ammonium carbonate as a precipitant for nickel in preparing the catalyst. By using potassium carbonate, however, a very effective catalyst was prepared in this laboratory. The results obtained by adding 18, 16, and 12 percent, respectively, of uranium oxide to nickel are shown in table 17.

TABLE 17. - Nickel-uranium oxide catalysts

(Catalyst contained 3 gm. Ni; gas velocity = 6 l./hr.;  
volume gas used in each test = 72.0 l.)

Experiment No.	U <sub>3</sub> O <sub>8</sub> content, percent of Ni in catalyst	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>	
				Gasoline (C <sub>5+</sub> )	Water
45A.....	18	180	88.6	144.8	188.2
45B.....	18	180	82.2	137.0	190.4
45C.....	18	185	88.0	148.0	198.0
45D.....	18	185-190	83.8	136.5	207.4
Average	18	180-190	86.9	141.6	196.0
46.....	16	190	78.5	137.5	202.3
47.....	12	190	76.8	135.8	189.0

Experiment No. 45. - This catalyst, nickel to which 18 percent uranium oxide had been added, showed extremely high activity during the first part of the experiment but deteriorated rapidly. At 180° C., a gas contraction of about 94 percent was indicated during the first 2 to 3 hours, but after 12 hours the contraction decreased to 82 percent; 144.8 ml. of gasoline (C<sub>5+</sub>) per cubic meter of synthesis gas was produced during this period. In this case, the ratio between the relatively heavy oil condensed in the burette, and the light oil absorbed by the activated carbon was 2.5:1. In addition, a small quantity of solid paraffin was deposited at the exit of the reaction tube during the last phase of the reaction, and this suggests a reason for the rapid

<sup>54/</sup> Brückner, H., and Jacobus, G., [The Activity of Nickel Catalysts in the Methane Synthesis]; Brennstoff Chem., vol. 14, 1933; pp. 265-268.

<sup>55/</sup> Work cited in footnote 31.

deterioration in catalyst activity. In experiment 45B, although the reaction proceeded at 180° C., the gas contraction decreased from 88.6 percent to 82.2 percent and the yield of gasoline from 144.8 to 137.0 ml./m.<sup>3</sup> of synthesis gas. Similarly, the reaction temperature had to be increased continuously in experiments 45C and D in order to maintain a suitable gas contraction. As a considerable quantity of solid paraffin had been deposited at the exit of the reaction tube when experiment 45 was concluded, the amount of uranium oxide was reduced from 18 percent to 16 percent to prevent formation of excessive amounts of high-molecular-weight hydrocarbons in future experiments.

Experiment No. 46. - Although the decrease in uranium oxide content succeeded in reducing the ratio of the production of relatively heavy oil to light oil from 2.5:1 to 1.8:1, a small quantity of solid paraffin was still found at the end of the reaction tube at the conclusion of this experiment.

Experiment No. 47. - The uranium oxide content was decreased still farther, to 12 percent, and a heavy oil-light oil ratio of about 1:1 was obtained. No solid paraffin was observed in the reaction tube. The durability of the catalyst was increased considerably at the expense of a lower reaction rate; from the standpoint of durability, therefore, 12 percent is considered the most suitable uranium oxide content.

#### Cobalt-Copper Catalysts

According to experimental results obtained by Fischer, when nickel and cobalt are used as catalysts for the production of liquid hydrocarbons, an extended hydrogen reduction at high temperature is necessary - 3 hours at 450° C. for nickel<sup>56/</sup> and 4 to 5 hours at 350° C. for cobalt.<sup>57/</sup> Use of this strenuous reduction procedure on an industrial scale, however, is uneconomical, not only because of the cost of the hydrogen but also because the high reduction temperature necessitates frequent maintenance of the reduction equipment. Therefore, a catalyst requiring no hydrogen reduction or one that requires only a short reduction at a relatively low temperature would be highly desirable. A method of attacking this problem was suggested by the fact that the reduction temperature of oxides of iron, nickel, and cobalt can be lowered considerably by the addition of a small quantity of readily reducible metals, such as platinum, palladium, copper, or silver.

Cobalt-copper catalysts were first used in the hydrocarbon synthesis by Elvins,<sup>58/</sup> Smith,<sup>59/</sup> and Kodama<sup>60/</sup> in early work on this problem. Copper, however, was first thought to be only a promoter, and the catalyst was normally used after hydrogen reduction at about 300° C. Fischer found later that the cobalt-copper catalyst did not require high-temperature hydrogen reduction and showed that reduction could be effected directly by synthesis gas at about 200° C.

<sup>56/</sup> Work cited in footnote 12.

<sup>57/</sup> Work cited in footnote 3.

<sup>58/</sup> Work cited in footnote 22.

<sup>59/</sup> Work cited in footnote 8.

<sup>60/</sup> Work cited in footnote 9.

Elvins<sup>61/</sup> considered Co-Cu-Mn catalyst the best, and Smith<sup>62/</sup> considered either Co-Cu-Mn or Co-Cu-U catalysts superior; Fischer<sup>63/</sup> designated 9 Co:1 Cu:2 Th as his standard catalyst; Fujimura and Tsuneoka<sup>64/</sup> obtained their highest yield of liquid hydrocarbons (145 ml./m.<sup>3</sup> of synthesis gas) by using 8 Co:1 Cu:0.2 Th:0.1 U catalyst. Cobalt-copper-catalysts have been prepared either by thermal decomposition of a mixture of the nitrate salts or by ignition with starches and cane sugar, as done by Fujimura;<sup>65/</sup> such silica substances as diatomaceous earth and pumice have been used as carriers.

Preparation of catalysts according to the methods described above resulted in widely varying activities because of variations in preparation conditions, and a constant yield of liquid hydrocarbons could not be obtained. By precipitation with alkaline carbonate according to Fischer,<sup>66/</sup> however, favorable results were obtained with nickel and cobalt catalysts.

### Experimental Procedure

Catalyst preparation. - To a cobalt nitrate solution corresponding to 3 gm. of cobalt were added a copper nitrate solution containing a definite amount of copper and nitrate salt solutions containing definite amounts of manganese, thorium, calcium, barium, lead, cesium, aluminum, and chromium. Three grams of diatomaceous earth was then mixed in, and slightly more potassium carbonate than required for neutralization was added. The precipitate was filtered, desiccated at about 100° C., and charged to the reaction tube. When uranium oxide and tungsten oxide were used as promoters, they were obtained by dissolving ammonium uranilate, obtained by adding uranium nitrate and ammonium to mixed carbonate salts of cobalt and copper and ammonium tungstate in concentrated nitric acid.

### Results

Effects of reduction temperature. - Fischer<sup>66/</sup> states that if 10 to 20 percent of copper is added to cobalt, the temperature of cobalt oxide is reduced from 350° C. to about 200° C. However, this is dependent on the type of catalyst used and the method of preparation. The resulting decreases in reduction temperature obtained by using 100 Co:10 Cu:12 U<sub>3</sub>O<sub>8</sub> and 100 Co:10 Cu:15 Mn catalysts are shown in tables 18 and 19.

61/ Work cited in footnote 22.

62/ Work cited in footnote 8.

63/ Work cited in footnote 21.

64/ Work cited in footnote 4.

65/ Work cited in footnote 36.

66/ Work cited in footnote 21.

TABLE 18. - Effect of the reduction temperature

(100 Co:10 Cu:12 U<sub>3</sub>O<sub>8</sub>:100 diatomaceous earth catalyst = 3 gm. Co;  
 reaction temperature = 210° C.; gas velocity = 6 l./hr.;  
 72.0 l. of gas used in each case)

Experiment No.	Reduction temperature, °C.	Reduction time, hours	Gas contraction, percent	Liquid products, ml./m <sup>3</sup>	
				Gasoline (C <sub>5+</sub> )	Water
4A.....	200	1	74.0	138.0	180.5
4B.....	200	3	76.2	140.2	195.2
4C.....	250	1	72.8	138.5	190.2

TABLE 19. - Effect of the reduction temperature

(100 Co:10 Cu:15 Mn:100 diatomaceous earth catalyst = 3 gm. Co;  
 gas velocity = 6 l./hr.)

Experiment No.	Reduction temperature, °C.	Reduction time, hours	Reaction temperature, °C.	Volume gas used, liters	Gas contraction, percent	Liquid products, ml./m <sup>3</sup>	
						Gasoline (C <sub>5+</sub> )	Water
48A.....	200	1	210	24.0	25.8	-	-
48B.....	200	1	220	24.0	30.0	-	-
48C.....	250	1	210	45.0	64.8	80.3	150.0
48D.....	250	3	210	43.0	70.2	108.5	168.5
48E.....	250	5	210	72.0	70.8	107.8	170.3

Virtually no change was found in the yield of gasoline (C<sub>5+</sub>) when Co:Cu:U<sub>3</sub>O<sub>8</sub> catalyst was reduced for 1 to 3 hours at 200° C. or for 1 hour at 250° C. In contrast to this, when Co:Cu:Mn catalyst was used, an unfavorable gas contraction was obtained with a hydrogen reduction of 1 hour at 200° or 250° C.; a desirable yield of gasoline was obtained only after hydrogen reduction for 3 to 5 hours at 250° C. To ascertain the reason for the different results produced by these low reduction temperatures, Co:Cu:U<sub>3</sub>O<sub>8</sub>:diatomaceous earth catalyst (100:10:12:100), which had been used in the synthesis for about 12 hours, was first air-oxidized at about 100° C. for an hour, followed by hydrogen reduction at 200° C. for an hour. When synthesis gas was then passed over the catalyst, the gas contraction was about 30 percent at 210° C., 35 percent at 220° C., and 50 percent at 230° C. Thereupon, hydrogen reduction was repeated at 250° C. for 1 hour, and a gas contraction of 68 percent was subsequently obtained at 210° C. It was not until the catalyst was reduced in hydrogen at 250° C. for 2 hours that the original activity finally was obtained. Thus, the good results obtained in experiments 4A, B, and C, table 18, appear to be a result of the reducing action of the ammonia gas released by the dissolution of ammonium uraniamate during the preparation of the catalyst, and the reduction of cobalt oxide containing 10 percent copper for 1 hour at 200° or 250° C. is not adequate. Indications are that reduction for more than 3 hours at 250° C. is necessary.

Fischer and Meyer<sup>67/</sup> showed that ammonia gas lowered the temperature at which catalysts could be reduced, suggesting that, if a mixture of hydrogen and ammonia gas were used instead of hydrogen alone, about an hour's reduction at 200° C. would be enough. To verify this suggestion, a bottle filled with approximately a 10 percent aqueous ammonia solution was placed before the reaction tube, and the hydrogen was bubbled through it. By reducing the catalyst with this hydrogen-ammonia mixture for 1 hour at 200° C., activity comparable to that resulting from hydrogen reduction for 3 hours at 250° C. was obtained.

Effect of quantity of copper added. - The decrease in reduction temperature of cobalt oxide, based on the easily reducible property of copper, depends on the amount of copper (relative to the cobalt) contained in the catalyst. However, according to experimental results obtained by Armstrong and Hilditch,<sup>68/</sup> Fischer,<sup>69/</sup> and Kodama,<sup>70/</sup> copper is not, itself, a catalyst for the synthesis of hydrocarbons from carbon monoxide-hydrogen mixtures. The function of copper, therefore, is merely to decrease the reduction temperature of cobalt oxide, or it may be thought of as acting as a type of promoter. (Fischer said that the production of cobalt carbide was accelerated by the reaction,  $\text{Co} + \text{Cu} + \text{CO} = \text{CoC} + \text{CuO}$ ). Hence, the addition of more than the optimum amount of copper would, in a manner analogous to other promoters, cover the active centers of the cobalt and decrease the activity.

The optimum amount of copper, therefore, is that which will decrease the catalyst reduction temperature while maintaining a gasoline yield equal to or greater than that obtained when the catalyst is reduced for 4 to 5 hours at 350° C. (without the addition of copper). The gasoline yields obtained from Co-Cu-U<sub>3</sub>O<sub>8</sub> catalysts (12 percent uranium oxide) containing various amounts of copper are shown in table 20.

From the gas contraction and the analyses of the synthesis and product gases shown in table 20, the rate of reaction between carbon monoxide and hydrogen and the percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons based on the carbon monoxide in the synthesis gas were obtained. The percentage of carbon monoxide converted to gasoline (C<sub>5+</sub>) was obtained by adding these three values and subtracting their sum from 100, with the results shown in table 21.

- 67/ Fischer, F., and Meyer, K., [The Activating Action of Ammonia Upon the Reduction and Activity of Nickel Catalysts]: *Brennstoff Chem.*, vol. 14, 1933, pp. 85-89.
- 68/ Armstrong, E. F., and Hilditch, T. P., Study of Catalytic Actions at Solid Surfaces X. The Interaction of Carbon Monoxide and Hydrogen as Conditioned by Nickel at Relatively Low Temperatures. A Practical Synthesis of Methane: *Proc. Roy. Soc. (London)*, vol. 103A, 1923, pp. 25-34.
- 69/ Fischer, F., Tropéa, H., and Dillthey, P., [The Reduction of Carbon Monoxide to Methane in the Presence of Various Metals]: *Brennstoff Chem.*, vol. 6, 1925, pp. 265-271.
- 70/ Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure I: Studies of the Catalytic Activity of a Few Metals by the Heating Curve Method]: *Jour. Soc. Chem. Ind. Japan*, vol. 52, 1929, p. 7; *Bull. Inst. Phys. Chem. Research (Tokyo)*, vol. 8, 1929, pp. 277-283; abstracts section (in German), vol. 2, 1929, pp. 35-36.

TABLE 20. - Effect of copper concentration.

(100 Co:12 U<sub>3</sub>O<sub>8</sub>:100 diatomaceous earth + Cu catalyst = 3 gm. Co; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used except as noted.)

Experiment No.	Cu content, percent of Co in catalyst	Composition of synthesis gas		Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./hr.		Product gas composition, percent						
		CO	H <sub>2</sub>			Gasoline (C <sub>5</sub> +)	Water	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub> +2	n.	iC <sub>4</sub>
49a	0	32.0	64.8	200	77.5	134.5	181.6	2.0	21.0	46.8	12.6	1.20	14.6	
50A	20	33.2	63.4	200	62.5	107.5	158.2	1.8	31.2	53.0	3.4	2.42	10.6	
50B	20	33.0	64.5	210	74.5	137.5	185.6	2.6	28.4	52.5	7.4	1.80	8.9	
3	10	32.6	64.0	200	60.4	110.6	150.5	2.5	30.0	56.1	2.4	2.97	8.9	
4	10	32.5	65.2	210	74.0	138.0	180.5	4.6	24.4	54.2	7.7	1.85	8.9	
18A	5	32.5	64.8	190	75.4	133.3	179.2	2.0	20.0	57.7	10.3	1.53	10.0	
18B	5	32.8	65.0	200	80.6	143.3	193.5	4.6	23.4	43.8	16.5	1.31	11.5	
51A	2.5	32.8	64.4	190	78.4	137.5	178.5	2.6	29.4	47.0	8.4	1.62	12.4	
51B	2.5	33.0	64.4	200	81.2	148.5	191.7	3.8	30.7	39.0	13.7	1.30	12.4	

a/ 154 l. of synthesis gas used.

TABLE 21. - Effect of copper concentration.

Experiment No.	CO conversion, percent	H <sub>2</sub> conversion, percent	Carbon distribution, percent of CO in synthesis gas		Gasoline (C <sub>5</sub> +)
			CO <sub>2</sub>	CO	
49	82.6	84.8	1.5	17.4	70.1
50A	64.8	68.7	2.0	35.2	53.5
50B	78.1	79.2	2.0	21.9	65.7
3	63.6	65.6	3.2	36.4	51.7
4	80.5	78.4	3.7	19.5	66.2
18A	84.9	78.1	1.5	15.1	71.5
18B	86.2	86.9	2.7	13.8	79.7
51A	80.6	84.2	1.7	19.4	70.0
51B	82.5	88.6	2.2	17.5	70.2



Experiment 49. - In accordance with the experimental results obtained by Fischer and Koch, hydrogen reduction for 4 to 5 hours at 350° C. resulted in a production of 137.5 ml. of gasoline per cubic meter of synthesis gas at 200° C. As the catalyst life increased (volume of gas used increased from 72.0 to 154.0 liters), the yield of gasoline decreased slightly to 132.0 ml./m<sup>3</sup>.

Experiments 50A and B. - This catalyst, containing 20 percent copper, was reduced for about 1 hour at 200° C., after which synthesis gas was introduced at the same temperature, with the production of 107.5 ml. of gasoline per cubic meter of synthesis gas. When the reaction temperature was raised to 210° C., this yield was increased to 137.5 ml./m<sup>3</sup>, essentially that obtained when the catalyst was reduced at 350° C. without the addition of copper.

Experiments 3, 4, and 16A and B. - The copper content was decreased to 10 percent and 5 percent in these experiments, and the catalysts were reduced at about 200° C. for an hour, after which synthesis gas was introduced. The yield of gasoline increased with decreasing copper content; a maximum of 143.3 ml./m<sup>3</sup> of synthesis gas was obtained at 200° C., when the copper content was 5 percent of the cobalt. This yield of gasoline is slightly more than that obtained in experiment 49, in which no copper was added.

Experiments 51A and B. - The copper content of the catalyst was decreased still further to 2.5 percent. After hydrogen reduction for about an hour at 200° C., synthesis gas was introduced. These conditions produced gasoline yields of 0 percent at 200°, 12 percent at 210°, and 80 percent at 220° C. After an hour's operation at 220°, the reaction temperature was lowered to 210° C., and the yield of gasoline remained at 80 percent. This demonstrates that reduction of cobalt oxide in hydrogen for 1 hour at 200° C. is completely ineffective when 2.5 percent of copper has been added. Accordingly, the catalyst was reduced in hydrogen at 250° C. for 1 hour in order to complete the reduction; gasoline yields of 137.5 and 145.3 ml./m<sup>3</sup> of synthesis gas were obtained at 190° and 200° C., respectively.

From these results, it appears that (1) the yield of gasoline (based on carbon monoxide in the synthesis gas) tends to increase with decrease in the content of copper relative to cobalt; (2) if mild reduction conditions are used, and if synthesis is to be started immediately after the reduction treatment, a copper content of more than 5 percent is necessary; and (3) a catalyst containing copper and which has been reduced for a short time at about 200° C. has a higher activity than a catalyst that has been reduced for a long time at 350° C. These points substantiate the theory that copper not only decreases the reduction temperature of cobalt oxide but also functions as a promoter for cobalt. It is still doubtful whether, as Fischer has stated, copper functions as a promoter in the production of cobalt carbide by the reaction  $\text{Co} + \text{Cu} + \text{C} = \text{CuO} + \text{CoC}$ .

Effect of promoters. - The effects of promoters were observed by adding 15 percent each of the following compounds (based on cobalt) to 100 Co:5 Cu catalyst: CaO, BaO, WO<sub>3</sub>, U<sub>3</sub>O<sub>8</sub>, CeO<sub>2</sub>, PbO, ZnO, ThO<sub>2</sub>, CaO, MnO, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MgO. The results found for U<sub>3</sub>O<sub>8</sub>, CeO<sub>2</sub>, ThO<sub>2</sub>, and MnO are shown in table 22; only these compounds exhibited any promoting effect.

TABLE 22. - The effect of promoters

(100 Co:5 Cu:15 promoter:100 diatomaceous earth catalyst = 3 gm. Co;  
gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Promoter	Reaction temperature, C.	Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>	
				Gasoline (C <sub>5+</sub> )	Water
52.....	GeO <sub>2</sub>	210	41.4	38.6	98.1
53.....	U <sub>3</sub> O <sub>8</sub>	200	80.8	150.5	212.0
54.....	ThO <sub>2</sub>	210	75.2	122.5	185.6
48D.....	MnO	210	70.2	108.5	168.5

Experiment 52. - Cerium oxide was first used as a promoter for cobalt-copper catalysts by Erdley and Nash,<sup>71/</sup> who observed that although the activity was large in the first stages of the reaction it decreased with time at an increasing rate. Kodama<sup>72/</sup> stated that cerium oxide was inferior to zirconia and magnesium oxide as a promoter for cobalt-copper catalysts. Experiment 52, using a catalyst in which cerium oxide was precipitated together with cobalt and copper as mixed carbonate salts, had a low activity and produced only 30.6 ml. of gasoline (C<sub>5+</sub>) per cubic meter of synthesis gas at 210° C.

Experiment 53. - Uranium oxide was used as a promoter for cobalt-copper catalysts by Smith, et al, and by Fujimura, et al. The author also found it to be very effective by adding it to nickel carbonate catalyst. In experiment 53, cobalt and copper were precipitated as mixed carbonate salts by potassium carbonate, and uranium oxide was precipitated as ammonium uranumate by ammonia. The catalyst thus prepared was very active. After hydrogen reduction for 1 hour at 200° C., 150.5 ml. of gasoline was obtained per cubic meter of synthesis gas at a reaction temperature of 200° C.; small quantities of solid paraffin were deposited at the end of the reaction tube in the final stages of the synthesis.

Experiment 54. - Co-Cu-ThO<sub>2</sub> catalysts were prepared by calcination by Kodama and Fischer and by precipitation by Watanabe. After 3 hours of hydrogen reduction at 250° C., a gas contraction of 75.2 percent was obtained at a reaction temperature of 210° and 122.5 ml. of gasoline was produced per cubic meter of synthesis gas. Although these results are inferior to those obtained with uranium, no solid paraffin was formed when thoria was used. The preparation of thoria-promoted catalysts require special precautions, however, as basic thorium carbonate may dissolve in excess potassium carbonate.

Experiment 48D. - Co-Cu-Mn catalysts were first studied by Smith and then by Fischer, who used a catalyst precipitated by sodium carbonate; a maximum gasoline yield of 118 ml./m.<sup>3</sup> of synthesis gas was obtained. The use of manganese as a promoter in experiment 48D, however, produced a gasoline yield of only 108.5 ml./m.<sup>3</sup> of synthesis gas after a hydrogen reduction at 250° C. for 3 hours, thus failing to reproduce the results obtained by Fischer et al.

The above results show that uranium oxide is the most satisfactory promoter and that thoria, manganese oxide, and cerium oxide are decreasingly effective in that order. Further studies of Co-Cu-U<sub>3</sub>O<sub>8</sub> catalyst were made on samples

<sup>71/</sup> Work cited in footnote 7.

<sup>72/</sup> Work cited in footnote 51.

containing 12 percent, 6 percent, and 3 percent uranium oxide, respectively, in an attempt to decrease the formation of solid paraffin as the formation of such material lowers the durability of the catalyst. The results are shown in table 23.

Experiments 55 and 56. - Decreasing the uranium oxide content from 15 percent to 12 percent, 6 percent, and 3 percent reduced the gasoline yield (after reduction for 1 hour at 200° C.) from 150.5 to 143.3, 137.5 and 95.6 ml./m.<sup>3</sup> of synthesis gas, respectively, at a reaction temperature of 200° C.

Consideration of the ratio between the relatively heavy oil condensed in the burette and the light oil absorbed by the activated carbon shows that production of light oil is favored by decreased quantities of uranium oxide, and that production of gaseous hydrocarbons is increased simultaneously. Thus, table 24 shows a heavy oil:light oil ratio of 2.3:1, 2.1:1, and 1.0:1 at uranium oxide contents of 15, 12, and 6 percent, respectively; the values listed in this table were calculated from the data given in table 23.

From table 24, it is evident that the conversion of carbon monoxide is about the same in all three cases. Hence, changes in the gasoline yield may be considered as dependent chiefly on the quantity of gaseous hydrocarbons produced. Although an increase in the production of gasoline would be desirable, any attempt to do this by increasing the heavy-oil production results in formation of an increasing quantity of solid paraffins.

The addition of manganese to Co-Cu-U<sub>3</sub>O<sub>8</sub> catalysts produced the results shown in table 25.

The percentages of carbon dioxide, carbon monoxide, gaseous saturated hydrocarbons, and gasoline in the product gases, based on the carbon monoxide in the synthesis gas, were calculated by the usual method and are shown in table 26.

Experiments 58, 59, and 60. - Addition of 16 and 8 percent manganese to 100 Co:5 Cu:12 U<sub>3</sub>O<sub>8</sub> catalyst accelerated the production of gaseous hydrocarbons and decreased the yield of gasoline. A manganese content of 4 percent, however, showed a promoting effect, increasing the gasoline yield from 143.3 to 153.2 ml./m.<sup>3</sup> of synthesis gas.

Experiment 61. - Decreasing the uranium oxide content to 6 percent produced essentially the same results obtained with a uranium oxide content of 12 percent. About 4 percent manganese was found to be most suitable, a large manganese content having an accelerating effect upon the production of gaseous hydrocarbons.

TABLE 23. - Effect of promoters

(100 Co:5 Cu:100 diatomaceous earth + U<sub>3</sub>O<sub>8</sub> catalyst = 3 gm. Co; reaction temperature = 200° C.; gas velocity = 6 l./hr.; 72.0 l. synthesis gas used in each case)

Experiment No.	U <sub>3</sub> O <sub>8</sub> , percent of Co in catalyst	Composition of synthesis gases, percent			Gas contraction, percent	Liquid products, ml./m. <sup>3</sup>		Product gas composition, percent						
		CO		H <sub>2</sub>		Gasoline (C <sub>5</sub> +)	Water	CO <sub>2</sub>	C <sub>m</sub> H <sub>n</sub>		H <sub>2</sub>	C <sub>m</sub> H <sub>n</sub> +2	n	N <sub>2</sub>
		CO	H <sub>2</sub>						C <sub>m</sub> H <sub>n</sub>	CO				
55	12	32.8	64.4	2.8	80.6	143.3	193.5	4.6	0.2	23.4	43.8	16.5	1.38	11.5
56	6	33.0	64.0	3.0	82.5	137.5	200.0	5.0	.4	20.8	31.9	26.3	1.20	15.1
57	3	33.0	63.8	3.2	62.4	95.6	166.5	1.0	.2	30.5	54.8	5.4	1.40	8.1

TABLE 24. - Effect of promoters

Experiment No.	CO conversion, percent	Carbon distribution, percent of CO in synthesis gas		
		CO <sub>2</sub>	CO	Gasoline (C <sub>5</sub> +)
53	85.2	2.2	14.8	10.9
55	86.2	2.7	13.8	12.8
56	89.0	2.7	11.0	17.1
57	65.2	1.1	34.8	8.6

TABLE 25. - Effect of promoters

(Gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Catalyst composition		Reaction temperature, °C.	Synthesis gas composition, percent			Gas contraction, percent	Liquid products, ml./m. 3		Product gas composition, percent						
	Co	Cu		U <sub>3</sub> O <sub>8</sub>	Mn	CO		H <sub>2</sub>	N <sub>2</sub>	Gasoline (C <sub>5</sub> +) Water	CO <sub>2</sub>	C <sub>m</sub> H <sub>n</sub>	CO	E <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub>	n
58	100	5	12	16	32.0	65.3	2.7	70.4	120.8	180.0	4.6	22.0	50.8	11.3	1.14	11.3
59	100	5	12	8	32.0	65.0	3.0	75.2	125.0	183.3	2.0	20.4	44.8	20.4	1.12	12.0
60	100	5	12	4	32.2	65.0	2.8	82.4	158.2	205.5	2.8	20.0	50.5	12.4	1.88	14.1
61	100	5	6	4	31.8	65.4	2.8	76.8	150.0	210.5	1.8	20.8	48.5	15.4	1.26	13.3

TABLE 26. - Effect of promoters

Experiment No.	Co conversion, percent	Carbon distribution, percent of CO in synthesis gas	
		CO <sub>2</sub>	CO
58	79.6	4.2	20.4
59	64.4	1.5	15.6
60	89.1	1.5	10.9
61	86.1	1.2	13.9