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FISCHER-TROPSCH SYNTHESIS IN A FLUIDIZED-CATALYST REACTOR WITH A NITRIDED, FUSED-IRON CATALYST

BY J. J. DEMETER AND M. D. SCHLESINGER

United States Department of the Interior — 1959

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FISCHER-TROPSCH SYNTHESIS IN A FLUIDIZED-CATALYST REACTOR WITH A NITRIDED, FUSED-IRON CATALYST[1/]

by

J. J. Demeter[2/] and M. D. Schlesinger[2/]

SUMMARY

As part of its work on converting coal to fluid fuels, the Federal Bureau of Mines has been studying the synthesis of liquid fuels from carbon monoxide and hydrogen by Fischer-Tropsch synthesis.

A fluidized bed of nitrided, fused-iron catalyst has been operated successfully to produce high yields of oxygenated compounds. Trouble-free operation continued for over 800 hours, and the test was terminated voluntarily. About 85 percent of the fresh feed was converted when the unit was operated at a space velocity of 500 $hr.^{-1}$, a 12:1 recycle-to-fresh-feed-gas ratio, a 300-p. s. i. g. pressure, and a temperature of 252° C. When operating at a fresh-feed-gas space velocity of 1,000 $hr.^{-1}$ and a 9:1 ratio of recycle to fresh gas, conversion of fresh feed was 68 percent, and the product yield was 235.9 grams per cubic meter of synthesis gas converted. The oxygenate and C_5 and heavier hydrocarbon yield was 110.6 grams per cubic meter of gas converted, 83 percent of this was oxygenates. The atom ratio of N:Fe of the catalyst, initially 0.455, decreased to 0.288 by the end of the 800-hour experiment. Nevertheless, the yield of oxygenated compounds per cubic meter of $H_2 + CO$ converted at the end of the run was approximately the same as that obtained 500 hours earlier with identical operating conditions. X-ray analysis of the discharged catalyst indicated that only ϵ-iron carbonitride was present. Sieve analysis of the discharged catalyst indicated that only 2 percent of fines was produced during the reduction, nitriding, and synthesis.

INTRODUCTION

In its study of methods for converting coal to fluid fuels, the Bureau of Mines developed an iron Fischer-Tropsch catalyst that was more resistant to oxidation and yielded a lighter product, richer in alcohols than that obtained in synthesis over known iron catalysts. Previously the fluid-bed process required relatively high temperatures to prevent agglomeration ("waxing up") of the catalyst by the product, yet these temperatures - above 300° C. - caused impediments, such as carbon deposition and catalyst oxidation. The

1/ Work on manuscript completed July 25, 1958.
2/ Chemical engineer, Bureau of Mines, Region V, Pittsburgh, Pa.

Bureau developed an iron carbonitride catalyst that offered the opportunity to avoid these difficulties by operating a fluid-bed process at considerably lower temperatures.

The catalyst-testing laboratory has shown[3] that a nitrided, fused-iron catalyst is more active than reduced iron and stable when operated below 275° C. Considerably higher yields of oxygenated compounds, predominantly alcohols, are produced with nitrided catalysts. Much of this alcohol might be advantageously blended with the gasoline, since a study[4] has shown that the octane increase resulting from adding 10 percent by volume of ethyl alcohol is about the same as that produced by adding 1 ml. of tetraethyl lead per gallon. Addition of 25 percent of alcohol is equivalent to 3 ml. of tetraethyl lead. An alcohol-rich gasoline (containing 28.4 weight-percent of C_1 - C_3 alcohols) had been produced with a nitrided, fused-iron catalyst in a pilot plant containing a reactor with a fixed catalyst bed that was cooled by oil circulation. The gasoline had a clear research octane number of 92.9, and adding 1 ml. of tetraethyl lead raised the octane number to 98.5. A gasoline produced with a nonnitrided, fused-iron catalyst in the same pilot plant had a clear research octane number of 84.8, which was increased to 91.2 by adding 1 ml. of tetraethyl lead.

Another advantage of using nitrided, fused-iron catalysts is that the liquid product is predominantly in the gasoline and diesel boiling range and thus reduces or eliminates the need for cracking heavy products to obtain a maximum gasoline yield. Although more C_1 and C_2 gases are obtained than with a reduced-iron catalyst, this is at least partly offset by the yield of these gases obtained when the heavy hydrocarbons produced with reduced-iron catalysts are cracked. The purpose of using a nitrided, fused-iron catalyst in a fluidized bed was to determine if the short contact time of the gas in the catalyst bed (as a result of the inherently high gas velocity) affected the yield of oxygenated compounds. If the primary product of the synthesis is alcohols (which are converted to olefins and paraffins by secondary reactions), short contact time should result in a higher yield of oxygenates, because the primary product is removed rapidly from the reaction zone.

ACKNOWLEDGMENT

The authors hereby express their appreciation to the many persons involved in acquiring the necessary information for this paper - in particular, the operating staff of the Gas Synthesis Section development laboratory, the Analytical Section, and the mass-spectrometer group.

DESCRIPTION OF APPARATUS

The multiple-feed, fluidized-catalyst reactor is shown schematically in figure 1. The reactor consists of a 1-inch Schedule 80 seamless steel

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3/ Anderson, R. B., and others, Studies of the Fischer-Tropsch Synthesis, VII. Nitrides of Iron as Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3502-3508.

4/ Porter, J. C., and Wiebe, R., Alcohol as an Antiknock Agent in Automotive Engines: Ind. Eng. Chem., vol. 44, 1952, pp. 1098-1104.

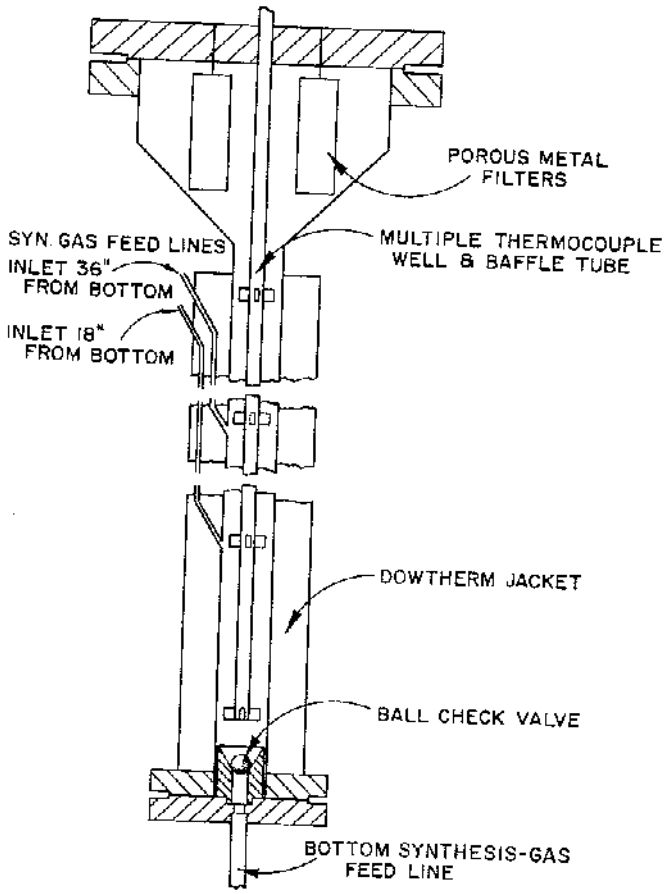

FIGURE 1. - Multiple-Feed Fluidized-Catalyst Reactor.

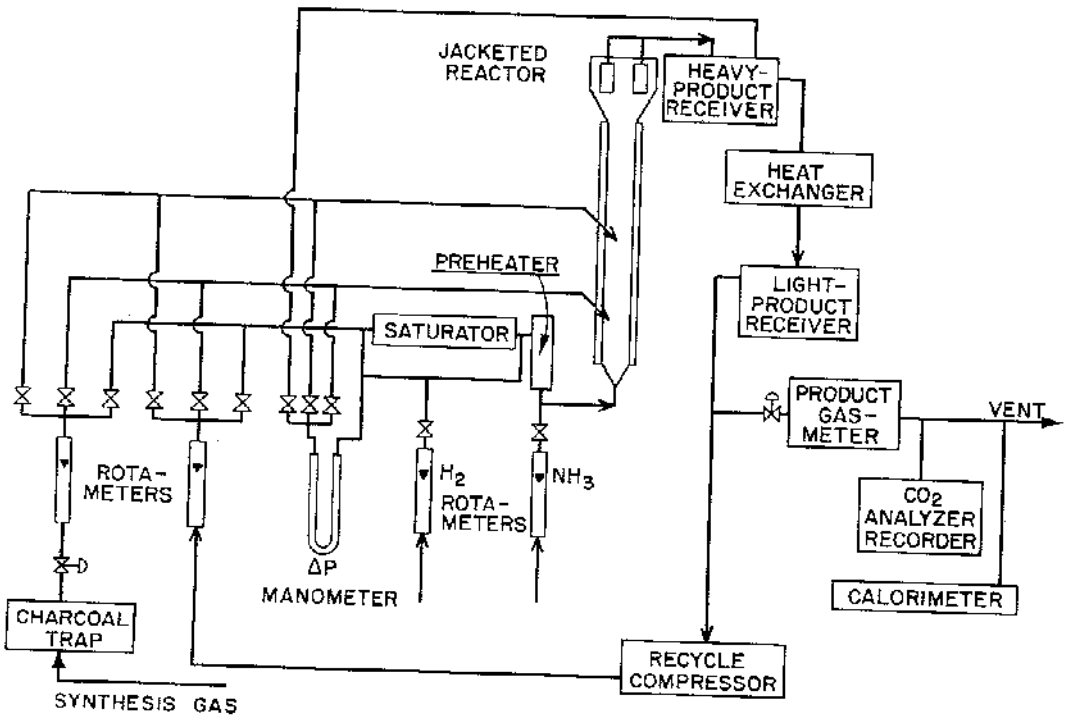

FIGURE 2. - Flow Diagram With Multiple-Feed Fluidized Bed.

pipe, 6 feet long, enclosed in a 3-inch Schedule 40 heat-exchanger jacket. A 3/8-inch-outside-diameter, internal-baffle tube with external fins is inserted in the center of the reactor tube to disperse the catalyst and aid in fluidization; it also serves as a thermowell for a five-junction thermocouple. The thermocouple junctions are placed at heights of 1, 8, 17, 35, and 60 inches above the bottom of the reactor. Three of the junctions are approximately at feed-gas inlet points - one at the bottom of the reactor, one 18 inches above the bottom, and one 36 inches above the bottom.

The reactor head is fitted with two porous stainless-steel filters to prevent carryover of small catalyst particles with the product gas. The filters are so arranged that one may be used to remove product gas while the other is being cleaned and cooled by a stream of blowback recycle gas. A ball valve at the bottom of the reactor prevents the catalyst from surging back into the inlet section of the unit. The catalyst is sampled through the bottom of the reactor during operation by displacing the ball with a rod passed up through a plug valve and allowing the catalyst to drop into a small-diameter capped pipe that extends below the bottom flange of the reactor.

The operating limits of the unit are approximately 480° C. and 300 p. s. i. g. For a maximum fluidizing velocity of 2 feet per second at these conditions, the total flow of gas is approximately 320 standard cubic feet per hour. A charge of 350 to 500 ml. of catalyst finer than 80-mesh fills the reactor to a height of 3 to 4 feet (settled bed).

The flow system for the unit is shown in figure 2. Synthesis gas at 400 to 500 p. s. i. g. is supplied from a high-pressure manifold through a main shutoff valve, an activated-charcoal purification unit, a pressure reducer, and a rotameter. The stream is then divided and passed through three throttle valves that control the flow to each gas-inlet point. Steam may be added to the synthesis gas by passing the bottom feed stream through an electrically heated saturator placed upstream from the preheater. Provision is also made to supply the system with hydrogen for reduction and ammonia for nitriding.

The temperature of the bottom feed-gas stream is controlled by an electrical preheater. The two upper feed-gas streams are introduced through tubes that run down through the Dowtherm-jacketed section of the reactor for preheating before they enter the side of the reactor. This design eliminates local overheating, since the heat liberated in any section comes from reaction of only part of the gas stream. The fresh feed gas entering at one point is almost completely converted by the time it reaches the next inlet point 18 inches above. In effect, the gas reaching each successive point is recycle gas. In these experiments using a nitrided, fused-iron catalyst it was not necessary to distribute the fresh-feed synthesis gas for temperature control. All of the fresh feed entered the bottom inlet, and the upper inlets were used for pressure-drop measurements. The multiple-feed feature was required when methane was synthesized over nickel catalysts at a high throughput.5/

5/ Greyson, M., Demeter, J. J., Schlesinger, M. D., Johnson, G. E., Jonakin, J., and Myers, J. W., Synthesis of Methane: Bureau of Mines Rept. of Investigations 5137, July 1955, 50 pp.

Gases pass overhead from the reactor through a trap system to recover solid and liquid products. Products that are solid at room temperature are recovered from a steam-jacketed product receiver, and the liquid hydrocarbons, oxygenates, and water are recovered from a water-cooled product receiver. The gas stream from the liquid-product receiver is split; one part goes to the recycle compressor and the other through a pressure reducer to a gas meter and to a recording carbon dioxide analyzer before being vented to the atmosphere. The recycled gas stream passes through a rotameter and then to three throttle valves that control the flow of the recycle gas to each inlet gas stream. A differential-pressure manometer is arranged to measure pressure drops between a point just before the preheater and the 18- and 36-inch gas-entry points and a point after the filters.

DESCRIPTION OF EXPERIMENTS

Two experiments, runs F-53 and F-54, were made in this fluidized system. Reduction and nitriding were effected in the synthesis reactor.

Run F-53

A fused-iron catalyst, D-3001, 80- to 230-mesh, was completely reduced to alpha iron with hydrogen at 400° to 410° C., 100 p. s. i. g., and a space velocity of 3,000 volumes of gas at S. T. P. per hour per volume of settled bed. Catalyst D-3001 is a synthetic-ammonia catalyst which has the composition shown in table 1.

TABLE 1. - Composition of catalyst D-3001

	Weight-percent
Fe	66.8
SiO_2	.6
Cr_2O_3	.8
MgO	4.6
K_2O	.6

The catalyst has a total surface area of 10 square meters per gram when reduced completely with hydrogen at 450° C. and 1,000 space velocity.6/ The reduced iron was then nitrided at atmospheric pressure and 325° to 350° C. with ammonia at a space velocity of 780 $hr.^{-1}$. During the nitriding operation a bleed stream of hydrogen was maintained through the middle and upper gas-inlet lines to keep them free of catalyst. The bleed streams of hydrogen evidently retarded the nitriding operation; the nitride produced was γ'-Fe_4N rather than the preferred $\epsilon'Fe_2N$.

Shortly after synthesis was initiated, failure of the recycle-gas compressor resulted in excessive catalyst temperatures that probably decomposed

6/ Hall, W. K., Tarn, W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. VIII. Surface-Area and Pore-Volume Studies of Iron Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5436-5443.

the small amount of nitride present. Attempts to operate the catalyst at 250° C. resulted in condensation of heavy hydrocarbons upon the catalyst. The wetted catalyst lost its fluidization properties, and the run was terminated.

Run F-54

Another batch of fused iron, D-3001, 120- to 230-mesh, was similarly reduced with hydrogen to alpha iron. The reduced iron was nitrided with ammonia at atmospheric pressure and 325° to 375° C. at a space velocity of 310 hr.$^{-1}$. During the nitriding operation bleed streams of helium instead of hydrogen were maintained through the middle and upper gas-inlet lines. This time the catalyst was predominantly ϵ-Fe_2N.

Because stepwise activation of the nitrided catalyst in slurry operations had resulted in higher yields of oxygenates and less $C_1 + C_2$ hydrocarbon gases,7/ a similar activation procedure was followed in the fluidized-bed experiments. This involved successive periods of operation at 100, 150, and 200 p. s. i. g. at low conversion levels - 17.7 to 24.4 percent.

After the catalyst activation (78 hours), synthesis was initiated at a fresh-feed space velocity of 3,000 hr.$^{-1}$, with a 3:1 recycle ratio of tail gas to fresh feed gas and 300 p. s. i. g. A conversion of 24.3 percent was obtained at 238° C. The temperature was raised to 250° to 253° C. to reach a higher conversion, and the space velocity was lowered stepwise from 3,000 to 500 volumes of gas per volume of catalyst per hour. The ratios of recycle to fresh feed varied from 3:1 to 12:1.

DISCUSSION OF EXPERIMENTS AND RESULTS

Experimental results are summarized in table 2. The product distribution was typical for a nitrided, fused-iron catalyst - high gas yields, low-boiling liquid hydrocarbons, and high yields of oxygenated products. The figures pertaining to gaseous products were calculated from mass-spectrometer analyses of 3 or 4 spot gas samples taken during each steady-state period. All of the liquid products were accumulated during a steady-state period and mixed. For steady-state periods VI to X (table 2) the liquid-hydrocarbon and oxygenate yield ranged from 94.2 to 120 grams per cubic meter of gas converted, and 76 to 87 percent of this was oxygenated. The maximum operating temperature was limited to approximately 255° C., as nitrided-iron catalysts decompose and lose nitrogen at an accelerated rate at higher temperatures. When the nitride is decomposed the catalyst gives products with a composition similar to that obtained from reduced iron.

During the experiment the recycle ratios were adjusted with each change in synthesis-gas rate to maintain a superficial linear velocity of 0.5 to 0.9 feet per second through the catalyst bed. Recycle-gas rates at the lower space velocities are undoubtedly greater than necessary and could be reduced if a reactor with greater height were used to contain a deeper catalyst bed.

7/ Schlesinger, M. D., Benson, H. E., Murphy, E. M., and Storch, H. H., Chemicals From the Fischer-Tropsch Synthesis. Ind. Eng. Chem., vol. 46, 1954, pp. 1322-1326.

TABLE 2. - Experiment F-54, operating co

Period	I, 4/22-4/23/55		II, 4/23-4/24/55		III, 4/24-4/25/55		IV, 4/25-4/29/55		V, 4/29-5/2/55		VI, 5/2-5/6/55	
Catalyst age ..... hours	0-30		30-54		54-78		78-168		168-240		240-336	
Converter pressure ..... p. s. i. g.	100		150		200		300		300		300	
Fresh-feed space velocity ..... hr.$^{-1}$	1,000		1,500		2,000		3,000		1,500		1,500	
Superficial linear velocity .. ft./sec.	0.9		0.9		0.9		0.9		0.8		0.8	
Recycle to fresh-gas ratio	3:1		3:1		3:1		3:1		6:1		6:1	
Average temperature ..... °C.	238		239		239		238		240		250	
Temperature differential ..... Do.	12		15		16		13		11		11	
Feed-gas ratio ..... H_2:CO	1:1		1:1		1:1		1:1		1:1		1:1	
Usage ratio ..... Do.	1.3:1		1.4:1		1.3:1		1.3:1		1.5:1		1.3:1	
H_2 conversion ..... percent	27.5		21.4		20.2		27.5		41.2		54.7	
CO conversion ..... Do.	21.4		15.2		15.1		21.2		28.1		42.1	
H_2 + CO conversion ..... Do.	24.4		18.3		17.7		24.3		34.6		48.4	
CO_2-free contraction ..... Do.	21.5		16.0		15.8		22.6		30.8		43.9	
Yield, gm./m.^{3} H_2 + CO converted:												
CH_4	43.65		44.39		52.91		34.87		47.25		47.52	
C_2	18.55	70.9	19.34	69.7	20.11	79.2	8.99	47.8	20.18	70.1	21.53	70
C_2=	8.73		6.00		6.20		3.95		2.66		1.64	
C_3	6.55		9.67		9.90		12.94		8.53		13.27	
C_3=	32.74		27.27		28.27		24.80		28.40		22.74	
C_4	18.55	86.2	12.67	88.1	13.15	63.6	17.25	66.5	11.34	70.7	7.05	52
C_4=	17.46		33.69		12.25		7.91		15.83		9.87	
C_5	-		-		-		-		-		-	
C_5=	10.91		14.80		-		-		6.64		-	
C_3 + C_4 olefins ..... weight-percent	66.7		73.2		63.8		52.0		69.0		61.7	
Oxygenated compounds in oil phase ..	-		-		-		-		-		33.7	
Oxygenated compounds in water phase.	48.0		45.8		46.9		33.8		56.1		66.1	
Total oxygenated compounds	-		-		-		-		-		99.8	
Unknown	-		-		-		-		-		4.3	
Hydrocarbons, condensed	-		-		-		-		-		15.9	
Total yield	-		-		-		-		-		243.6	
Water	69.7		101.8		130.0		96.2		127.7		103.3	
Carbon dioxide	402.7		260.2		259.6		163.9		223.5		289.3	
Recovery ... weight-percent of feed gas	103.4		100.2		101.0		93.5		100.6		101.1	
Partial pressure, H_2 in inlet gas ..... p. s. i. g.	-		-		-		145.6		130.4		117.8	
Infrared analysis of oil phase ..... weight-percent (-OH)	-		-		-		-		-		12.5	

Near the end of the run the unit was operated at a space velocity of 500 volumes per volume per hour, a recycle ratio of 12:1, and a pressure of 300 p. s. i. g. About 85 percent of the synthesis gas was converted at these conditions. Twenty-four hours before the experiment was ended the fresh-feed space velocity was increased to 1,000 volumes per volume per hour to duplicate run conditions employed 500 hours earlier. The conversion of synthesis gas had decreased from 68 percent obtained previously at 1,000 $hr.^{-1}$ space velocity to 61 percent, but the yield of oxygenated compounds per cubic meter of $H_2 + CO$ converted was approximately the same as that obtained 500 hours earlier. This yield was obtained despite the decrease of the N:Fe atom ratio of the catalyst from 0.455 to 0.228 during the total experiment.

The sieve analyses of the raw catalyst charged to the reactor and of the catalyst discharged after 837 hours of synthesis are shown in table 3. Comparison of the sieve analyses shows that catalyst breakdown due to attrition and other causes was very small. The percentage of fines (catalyst passing through a 230-mesh sieve) was increased from 1.6 to only 3.9 percent during reduction, nitriding, and synthesis. The expansion in particle size that occurs when reduced iron is nitrided[8/] is indicated by the increased amounts of the catalyst in the 100- to 140- and 140- to 170-mesh ranges and the decreased amount of catalyst in the 170- to 200- and 200- to 230-mesh ranges.

TABLE 3. - Sieve analysis of raw and discharged catalyst

Tyler standard-sieve size, mesh	Raw catalyst, weight-percent	Discharged catalyst, weight-percent
100-140	31.9	45.1
140-170	18.9	25.4
170-200	32.8	21.3
200-230	14.8	4.3
>230	1.6	3.9

The chemical analysis of the discharged catalyst is shown in table 4. An X-ray analysis indicated that only ϵ-iron carbonitride was present. The sample was analyzed for total carbon, and the amount of free carbon was calculated by subtracting the amount of carbon found as Fe_2C and as hydrocarbons. Although the partial pressure of hydrogen in the inlet gas was only 59 to 88 pounds per square inch (while operating at 300 p. s. i. g.) during the last 500 hours of operation, the production of free carbon was negligible. The discharged catalyst had a metallic luster, which further indicated the absence of any large amount of elemental carbon. The mechanical stability of the catalyst during the experiment may have been due to the absence of extensive carbon and iron oxide formation. Similar conclusions were published by the Fuel Research Board.[9/]

8/ Stein, K. C., Thompson, G. P., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XVII. Changes of Iron Catalysts During Pretreatment and Synthesis: Jour. Phys. Chem., vol. 61, 1957, pp. 928-932.

9/ Department of Scientific and Industrial Research, Fuel Research, 1951: Her Majesty's Stationery Office, 1952, p. 17.

TABLE 4. - Chemical analysis of discharged catalyst

	Weight-percent
Iron	76.04
Nitrogen	4.04
Sulfur	(1/)
Potassium oxide	.23
Carbon:	
As Fe_2C	4.71
As hydrocarbons	3.16
Free carbon 2/	2.02
Hydrogen as hydrocarbons	.53
Structural promoters and impurities	6.80
Oxygen 2/	2.47

1/ None detected.
2/ By difference.

The presence of 3.7 percent hydrocarbons condensed on the catalyst may have been responsible for the slight loss in activity noted near the end of the experiment when operating conditions of 500 hours earlier were duplicated. A slow but gradual buildup of pressure drop across the filters was noted after the superficial linear velocity of the gas through the reactor was lowered to 0.74 foot per second in period VIII. Examination of the filters after the run indicated the presence of hydrocarbons condensed on the surface of the porous stainless-steel filters. After the hydrocarbons were removed by steaming, the pressure drop across the filters returned to normal. Higher operating temperature on the filter probably would prevent condensation of hydrocarbons on the surface during synthesis.

The oxygenated products were recovered from an aqueous layer containing the compounds of lower molecular weight and an oil layer containing the compounds of higher molecular weight. There was some overlap of the oxygenated compounds in each of the layers because of the mutual solubility of some oxygenated compounds in both water and oil. The amount of oxygenated material in the aqueous layer was determined by the mass spectrometer and indirectly by the Karl Fischer reagent. The mixture of hydrocarbons and oil-soluble, oxygenated compounds was distilled into six fractions, which were analyzed for functional groups by the infrared spectrometer.

The distribution of the various alcohols in the aqueous-product layer, as percent of the total alcohols found in the aqueous layer, is shown in figure 3. The percentage of methanol (14 to 20) was high as compared with less than 1 percent in the aqueous product from synthesis in a fluidized bed of reduced mill scale.10/ Ethyl alcohol represented 40 to 48 percent of the alcohols, the C_3 alcohols represented 20 to 30 percent, and each of the C_4 to C_6 alcohols was 4 to 8 percent of those in the aqueous phase. The shape of

10/ Morrell, C. E., Carlson, C. S., McAteer, J. H., Robey, R. F., and Smith, P. V., Jr. Products From Hydrocarbon Synthesis. Ind. Eng. Chem., vol. 44, 1952, pp. 2839-2843.

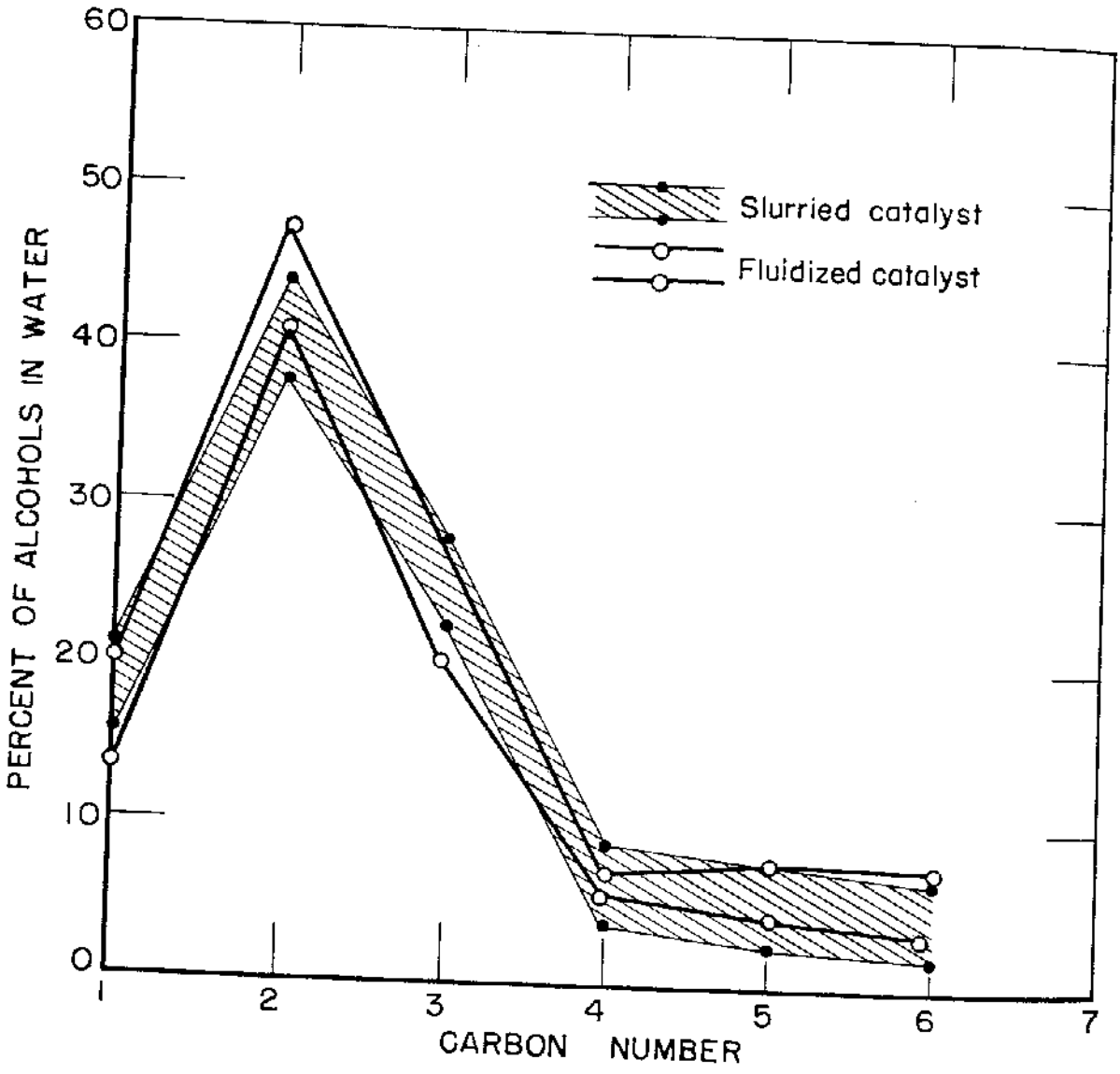

FIGURE 3. - Alcohol Distribution in Aqueous Phase.

the curve and analysis of the product oil show that some alcohols above C_6 also were present. A mass-spectrometer analysis of the trimethyl-silyl-ether derivatives of the aqueous-phase alcohols obtained during steady-state period VIII indicated that approximately 2 percent of the alcohols were C_7's and C_8's. Although the space velocity varied from 1,500 to 500 volumes per volume per hour and the synthesis-gas conversion ranged from 48 to 85 percent, the alcohol distribution in the aqueous phase remained relatively constant. The alcohol distribution in the aqueous product obtained with a nitrided-iron catalyst in a slurry-type synthesis unit[11/] is also shown in figure 3. Although the slurry unit was operated at lower space velocities (200 to 500 volumes per volume per hour) with 72- to 22-percent conversion of synthesis gas, the alcohol distribution obtained in the aqueous-product layer of the slurry unit approximates the distribution obtained in the fluidized unit. The aqueous layer produced in both the slurry and fluidized-catalyst units also contained small quantities of acetone, methyl ethyl ketone, methyl propyl ketone, and probably other oxygenated compounds that could not be detected because of their low concentrations. Titration with potassium hydroxide indicated an acid equivalent of approximately 0.2 to 0.9 percent of acetic acid in the aqueous-product layer.

The oil layer contained some light oxygenated compounds but mostly oxygenates of higher molecular weight. The oil was distilled into 6 fractions (initial boiling point to 100° C., 100° to 150° C., 150° to 200° C., 200° to 250° C., 250° to 300° C., and >300° C.). Each fraction was analyzed by an infrared spectrometer for functional groups. The percentages of oxygenated compounds in each fraction were estimated by the method of Anderson, Feldman, and Storch.[12/] The specific yields of oxygenated compounds in the oil and aqueous phases, in grams per cubic meter of $H_2 + CO$ converted, are shown in table 5. The content of oxygenated compounds in the oil phase and the total yield of oxygenated compounds increased with increased space velocity.

The oil-soluble oxygenates reported by Cain, Weitkamp, and Bowman[13/] from a fluidized bed of reduced mill scale was 25 to 30 percent of the oil - about one third of them alcohols. In the present experiments with a nitrided, fused-iron catalyst, 33 to 69 percent of the condensed-oil product was oxygenates; about 85 to 90 percent of this was alcohols and the remainder predominantly aldehydes or ketones, esters, and a small amount of acids. Most of the oil-soluble oxygenates occurred in the 1 to 4, 4 to 7, and 6 to 9 carbon-number fractions, with much smaller yields in the 9 to 11 and 11 to 13 carbon-number fractions. The water-soluble oxygenate yield in periods VI to X under steady-state conditions ranged from 55 to 66 grams per cubic meter of synthesis gas converted, and about 95 percent of this was alcohols. The sum of the water- and oil-soluble oxygenate yields ranged from 74.5 to 99.8 grams per cubic meter of gas converted, and the alcohol yields supplied 71 to 81 percent of

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11/ Work cited in footnote 7, page 7.

12/ Anderson, R. B., Feldman, J., and Storch, H. H., Synthesis of Alcohols by Hydrogenation of Carbon monoxide: Ind. Eng. Chem., vol. 44, 1952, pp. 2418-2424.

13/ Cain, D. G., Weitkamp, A. W., and Bowman, N. J., Oil-Soluble Oxygenated Compounds: Ind. Eng. Chem., vol. 45, 1953, pp. 359-362.

the total. The oxygenate yield reported by Chang Ta Yu, et al.[14], from a fluidized bed of nitrided, fused-iron catalyst was considerably lower than the yields mentioned above; the oxygen content of the liquid-hydrocarbon layer was about 1 percent, and the water-soluble oxygenates never exceeded 10 percent of the C_3+ yield.

Figure 4 shows that the $H_2 + CO$ percent conversion decreased with increasing fresh-feed space velocity at constant temperature and that the yield of oxygenated compounds per cubic meter of $H_2 + CO$ converted increased with increasing space velocity and decreasing conversion. The yield of $C_3 + C_4$ hydrocarbons (table 2) and the percentage of unsaturated $C_3 + C_4$ hydrocarbons also decreased with increasing conversion.

In periods VIII, IX, and X the fresh-feed space velocity was held constant at 750; the recycle ratio was set at 8:1, 10:1, and 12:1, giving superficial linear velocities of 0.5, 0.6, and 0.74 foot per second, respectively. As the recycle ratio and the superficial linear velocity of gas through the catalyst bed increased, the yield of oxygenated material increased in the oil phase and decreased in the aqueous phase. The total yield remained constant at approximately 74.5 grams per cubic meter of $H_2 + CO$ converted. The effect of recycle ratio on oxygenated-product yield is shown in figure 5. The recycle ratio, within the range studied, did not appear to affect the percent conversion of $H_2 + CO$.

In table 6 product yields obtained with nitrided, fused-iron catalysts in various types of reactors - fluidized catalyst bed, slurried catalyst, and oil-circulation fixed catalyst bed - are compared. The comparison was made at 68- to 69-percent conversion of 1:1 synthesis gas at 300-p. s. i. g. pressure. The fresh-feed space velocity, recycle ratio, and temperature of operation differed for each of the reactors, with the greatest difference for the fluid-bed reactor. The specific yield of oxygenated compounds obtained in the fluid-bed unit is much higher than the yields obtained in the other two units: 89.2 grams, compared with 68.0 and 46.6 grams per cubic meter of $H_2 + CO$ converted. Although the yield of liquid hydrocarbons was lower, the sum of the yields of oxygenated compounds plus liquid hydrocarbons obtained with the fluid-bed unit was still considerably greater than the yields obtained in the slurry and oil-circulation fixed-bed units - 102.7, 88.6, and 82.1 grams per cubic meter of $H_2 + CO$ converted, respectively. The sum of the products (excluding water and carbon dioxide) is 232 grams per cubic meter of $H_2 + CO$ converted in the fluidized bed and 207 and 198 grams in the slurry and oil-circulation fixed-bed units, respectively. A higher yield of useful products is obtained in the fluid-bed unit, because the products contain a higher percentage of oxygen; approximately 318 grams of oxygen per cubic meter of $H_2 + CO$ converted is consumed in making water and carbon dioxide in the fluidized unit, and approximately 364 and 403 grams of oxygen per cubic meter of $H_2 + CO$ converted are consumed in making water and carbon dioxide in the slurry and oil-circulation fixed-bed units, respectively. As higher space velocities and recycle ratios favor production of oxygenated compounds, the three types of reactors could be compared better if these variables were maintained at approximately the same values; however, the operating characteristics of the slurry and oil-circulation units limit them to considerably lower space velocities and recycle ratios than those employed in a fluidized catalyst unit.

14/ Ta-Yu, Chang, Nan-Tsuen, Leo, and Chun-Hao, Chang, Report on Pilot-Plant Synthesis of Liquid Fuels. Chem. Eng. Prog., vol. 54, No. 3, March 1958, pp. 55-58.

TABLE 5. - Liquid-product analysis, run F-54

Period		VI	VII	VIII	IX	X	XI	XII
Fresh-feed space velocity .....hr.$^{-1}$		1500	1000	750	750	750	500	1000
Superficial linear velocity ... ft./sec.		0.8	0.75	0.74	0.6	0.5	0.5	0.75
Average temperature ..... °C.		250	251	252	252	252	252	253
Recycle ratio		6:1	9:1	12:1	10:1	8:1	12:1	9:1
H_2 + CO conversion ..... percent		48.4	68.0	78.3	80.0	77.7	84.9	60.8
Oxygenated compounds in aqueous products, gm./m.^{3} converted:								
C_1OH		2.1	9.8	8.6	8.5	8.3	7.6	11.0
C_2OH		29.6	27.7	22.9	25.6	26.7	24.8	26.6
C_3OH		12.3	12.0	15.0	12.2	13.5	12.9	10.1
C_4OH		3.7	3.5	3.2	3.5	4.2	4.0	4.1
C_5OH		2.9	3.0	2.5	3.8	4.9	3.7	
C_6OH		2.1	2.5	1.9	3.5	4.2	3.2	
Acetone		2.6	2.0	1.5	1.8	1.8	1.4	2.1
Methylethyl ketone		.8	.9	.4	.6	.6	.5	.7
Methylpropyl ketone		.3	.4	.2	.4	.4	.4	.3
Total water-phase oxygenated compounds		66.1	61.7	55.1	59.7	65.0	51.8	67.2
Alcohols in H_2O-soluble oxygenates .... percent		94.4	95.0	96.2	95.5	95.7	96.2	95.4
Oxygenated compounds in oil phase, gm./m.^{3} converted[1]	Carbon No.							
I.B.P. 100° C.	1-4	15.0 (13.1)	13.7 (12.1)	9.4 (8.4)	5.5 (4.9)	3.9 (3.4)		
100°-150° C.	4-7	8.3 (7.8)	8.6 (8.0)	7.2 (6.6)	5.6 (5.2)	3.5 (3.1)		
150°-200° C.	6-9	7.0 (6.1)	5.6 (5.1)	2.6 (2.1)	3.1 (2.8)	1.6 (1.3)		
200°-250° C.	9-11	1.6 (1.3)	1.0 (0.7)	0.1 (0.08)	0.7 (0.6)	0.5 (0.4)		
250°-300° C.	11-13	1.4 (1.0)	1.3 (1.0)	0.3 (0.2)	0.5 (0.4)	0.3 (0.2)		
>300° C.	13+	0.4 (0.0)						
Total oil phase oxygenated compounds		33.7	30.2	19.5	15.4	9.5		
Oxygenates in oil phase ..... percent		62.5	68.5	44.7	45.7	32.5		
Total oil + water-phase oxygenated compounds		99.8	91.9	74.6	75.1	74.5		
Oxygenates in condensed product (less H_2O) ..... percent		83.2	86.8	76.2	80.4	79.2		
Alcohols in condensed product (less H_2O) ..... percent		72.9	80.7	71.3	75.7	75.0		

1/ Figures in parenthesis are alcohols.

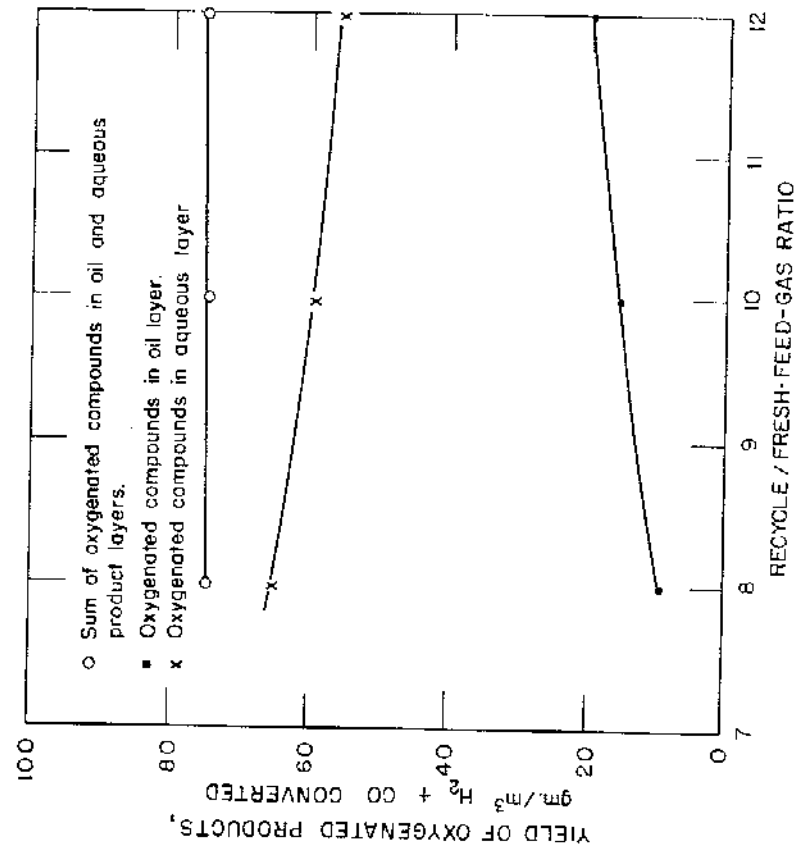

FIGURE 5. - Yield of Oxygenated Compounds As a Function of Recycle Ratio; H_2 + CO Conversion 78 to 80 Percent at 750 Space Velocity, 252°C. and 300 p.s.i.g. Pressure.

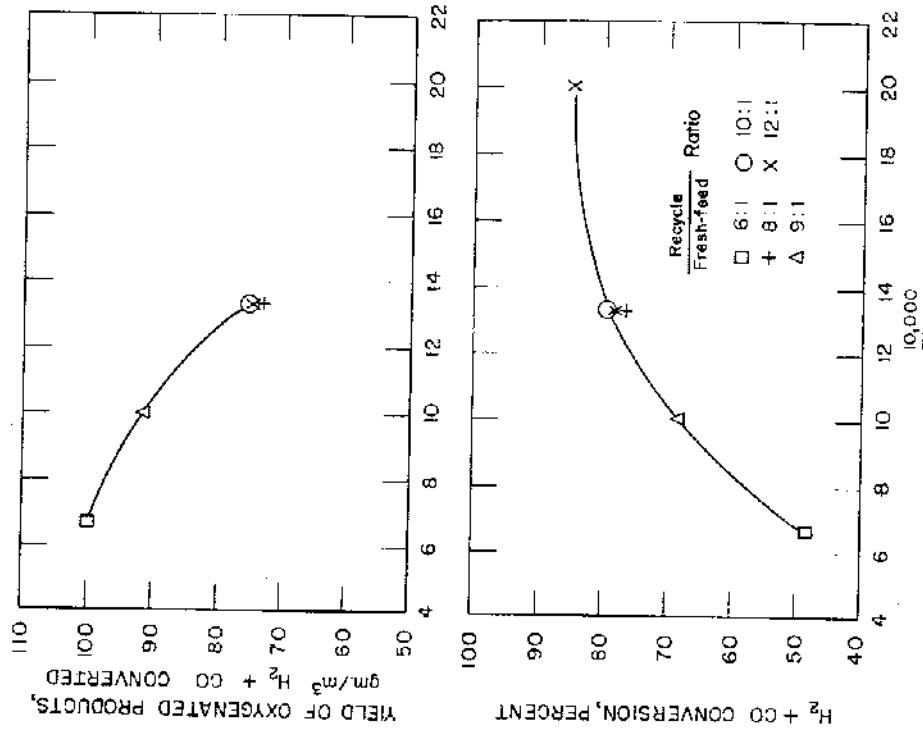

FIGURE 4. - H_2 + CO Conversion and Oxygenated Compounds Yield As a Function of Fresh-Feed Space Velocity (S); Pressure and Temperature Constant.

TABLE 6. - Comparative product yields obtained with nitrided, fused-iron catalysts in various types of reactors

Reactor type	Fluidized catalyst bed	Slurried catalyst	Oil-circulation, fixed catalyst bed
Pressure ..... p. s. i. g.	300	300	300
Temperature ..... °C.	251	247	230
Space velocity ..... $hr.^{-1}$	1/ 1000	2/ 100	3/ 200
H_2 + CO conversion ..... percent	68.0	69.2	68.7
Recycle ratio	9:1	2.06:1	1:1
Usage ratio ..... H_2:CO	1.2	0.95	0.75
Yield, gm./$m.^3$ H_2 + CO converted:			
$C_1 + C_2$	72.0	59.8	58.0
C_3 + gases	54.0	58.8	58.0
Oxygenated compounds in oil phase ..	29.4	30.4	5.8
Oxygenated compounds in water phase.	59.8	37.6	40.8
Total oxygenated compounds	89.2	68.0	46.6
Hydrocarbons (liquid)	13.5	20.6	35.5
Total liquid hydrocarbons plus oxygenated compounds	102.7	88.6	82.1
Total products 4/	232.1	207.2	198.1
Water	88.2	64.6	16.3
Carbon dioxide	328.5	422.0	535.0
Gram moles $H_2O/m.^3$ gas converted	4.90	3.59	0.91
Gram moles $CO_2/m.^3$ gas converted	7.47	9.23	12.16
Oxygenated compounds, percent of oxygenated compounds plus liquid hydrocarbons	86.9	76.7	56.8

1/ Based upon settled-bed volume.
2/ Based upon slurry volume.
3/ Based upon fixed-bed volume.
4/ Except H_2O and CO_2.
Note: Weight balances corrected to 100 percent for all 3 reactors.

CONCLUSIONS

Use of a fluidized bed is well suited for synthesis of highly oxygenated products with a nitrided-iron catalyst. The high linear velocity of gas through the reactor and the consequently short time of residence favors the production of high yields of oxygenates (up to about 85 percent of the C_3+ products). Because the nitrided catalysts decompose, with loss of nitrogen, at high temperatures, a maximum synthesis temperature of about 250° C. is recommended. Reduced or carbided-iron catalysts could not be operated in a fluidized bed at this temperature because high-boiling hydrocarbons form and coat the catalyst, causing loss of fluidization; however, virtually no high-boiling materials are produced with nitrided catalysts, even at relatively low synthesis temperatures, and fluidization of the particles is readily maintained. Although the synthesis was conducted with a feed gas having a H_2:CO ratio of 1:1, catalyst deterioration and the production of free carbon were negligible. When reduced or carbided-iron catalysts are used in a fluid-bed reactor, a hydrogen-rich synthesis gas is employed to minimize formation of free carbon and deterioration of catalyst.

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