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THE FISCHER-TROPSCH SYNTHESIS IN THE OIL-CIRCULATION PROCESS: EXPERIMENTS WITH A NITRIDED FUSED-IRON CATALYST

By D. Bienstock, J. H. Field, A. J. Forney,
J. G. Myers, and H. E. Benson

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UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

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ILLUSTRATIONS

TABLES (Con.)

THE FISCHER-TROPSCH SYNTHESIS IN THE OIL-CIRCULATION PROCESS: EXPERIMENTS WITH A NITRIDED FUSED-IRON CATALYST[1]

by

D. Bienstock,[2] J. H. Field,[3] A. J. Forney,[2]
J. G. Myers,[4] and H. E. Benson[5]

SUMMARY

Using a nitrided fused-iron catalyst, the Bureau of Mines investigated the Fischer-Tropsch reaction in the oil-circulation process. The nitrided iron was quite stable and permitted the longest run obtained thus far in the oil-circulation process without the need for reactivating the catalyst--3,700 hours of operation. The effects of several operating variables--temperature, pressure, gas-recycle ratio, space velocity, synthesis-gas composition, and synthesis with and without reflux of oil to the reactor--on the production of oxygenates were studied. The importance of removing reflux oil and of high gas recycle in increasing the oxygenate content was shown. A finished gasoline containing 28 percent by weight alcohols was produced. The research octane number (RON) was 92.9 clear, increasing to 98.5 with the addition of one milliliter of tetraethyl lead (TEL).

INTRODUCTION

The Federal Bureau of Mines has been engaged since 1944 in a research and development program on the synthesis of gasoline from coal. Gasification of coal with steam and oxygen to yield a "synthesis gas"--a mixture of carbon monoxide and hydrogen-- is being investigated at Morgantown, W. Va., and the synthesis of gasoline by catalytically reacting carbon monoxide and hydrogen over iron by the Fischer-Tropsch reaction is being investigated at Bruceton, Pa.

The historical background, catalytic development, and kinetics of the Fischer-Tropsch synthesis have been extensively covered.[6, 7] Recently the

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[5] Former chief, Gas Synthesis Section, Bureau of Mines, Region V, Pittsburgh, Pa.
[6] Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer-Tropsch and Related Syntheses: John Wiley & Sons, Inc., New York, N. Y., 1951, 610 pp.
[7] Emmett, P. H., Catalysis: Reinhold Publishing Corporation, New York, N. Y., vol. 4, 1956, 570 pp.

Bureau demonstrated a method for synthesizing a gasoline rich in alcohol.[8] Nitriding metallic iron with ammonia produces a catalyst that not only is more active than the conventionally reduced iron in the Fischer-Tropsch synthesis, but also gives considerably increased yields of oxygenated compounds, predominantly alcohols. These tests were conducted in a bench-scale reactor using a fixed bed of catalyst.

A study of the blending properties of alcohol in increasing the octane rating of gasoline used in automotive engines has been reported.[9] The effects of addition of alcohol and TEL on several gasoline stocks were compared. Addition of 10 volume-percent ethyl alcohol is about equivalent to 1 milliliter of TEL per gallon of gasoline; 25 percent is about equivalent to 3 milliliters.

To study the use of the nitrided catalyst on a larger scale, a pilot-plant investigation was undertaken using the oil-criculation process,[10] one of several processes under development by the Bureau for the synthesis of liquid fuels. In the oil-circulation process the large exothermic heat of reaction--7,200 B.t.u. per pound of product--in the Fischer-Tropsch synthesis is removed as sensible heat in the recycle oil, which completely submerges the catalyst. In a large unit the sensible heat of the recycle oil would be removed externally in a waste-heat boiler; in the smaller pilot-plant unit employed the heat is lost through radiation to the surroundings. Because the catalyst is completely submerged in the oil, close temperature control can be achieved, contributing to long catalyst life.

The objectives of this experiment were to study the activity and durability of a nitrided fused iron in the oil-circulation process and to prepare enough products to determine the yield and quality of a finished synthetic gasoline rich in alcohols.

EXPERIMENTAL PROCEDURE

Catalyst Preparation

Reduction

A batch of 46.10 pounds (0.297 cubic foot) of a 6- to 10-mesh synthetic magnetite was charged to the reduction unit. The unit is shown in figure 1. Chemical analysis of the magnetite is given below:

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[8] Anderson, R. B., Schultz, J. F., Seligman, B., Hall, W. K., and Storch, H. H., Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3502-3508.

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

[10] Benson, H. E., Field, J. H., Bienstock, D., Nagel, R. R., Brunn, L. W., Hawk, C. O., Crowell, J. H., and Storch, H. H., Development of the Fischer-Tropsch Oil-Recycle Process: Bureau of Mines Bull. 568, 1957, 72 pp.

	Weight-percent
Iron	67.3
Removable oxygen	25.7
Inerts:	
K_2O	0.34
MgO	4.5
SiO_2	0.99
Cr_2O_3	0.54
Total	99.37

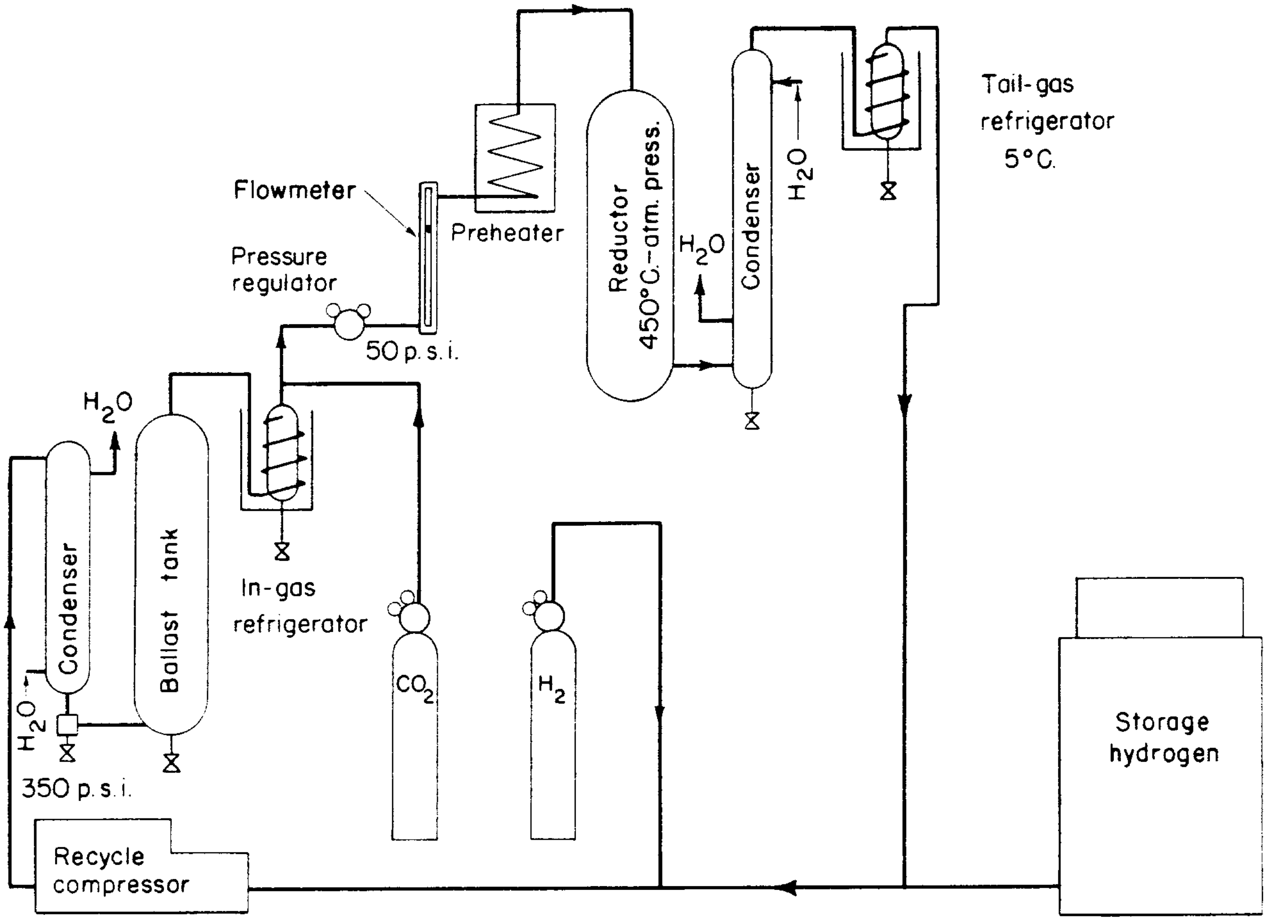

FIGURE 1. - Unit for Reducing Magnetite for Fischer-Tropsch Synthesis.

Hydrogen at atmospheric pressure was recycled through the bed at an hourly space velocity of 2,000 vol./vol.-hr. Space velocity is defined as the volume of gas at 0° C. and 760 mm. per hour per volume of catalyst. The temperature was increased from 160° to 450° C. during the first 16 hours and then maintained between 450° and 460° C. for 48 hours. Water was removed from the hydrogen by condensation through compression and refrigeration. The reduced catalyst was cooled to room temperature by circulating hydrogen through it.

The catalyst is highly pyrophoric and must be kept under an inert atmosphere, such as carbon dioxide, to prevent reoxidation. The catalyst was stored and transferred from the reduction to the nitriding unit by means of transfer vessels containing an inert atmosphere and provided with valves for charging and discharging the catalyst. Based on a weight loss of 11.77 pounds (25.5 percent of original charge) the reduction of iron oxide to metallic iron was calculated to be complete.

Nitriding

A charge of 33.92 pounds of reduced magnetite was then placed in the nitriding unit shown in figure 2. A horizontal reactor was employed with a relatively shallow bed of catalyst to provide space for expansion during the nitriding. Anhydrous ammonia gas, heated in a Dowtherm boiler to avoid overheating and minimize thermal cracking, was passed through the catalyst at atmospheric pressure and at an hourly space velocity of 500 vol./vol.-hr. To allow intimate and uniform contact with the catalyst, the ammonia was admitted through a perforated tube placed at the bottom of the reactor. The temperature of the bed was increased from 115° to 300° C. during the first 4 hours and then maintained at 300° to 326° C. for the next 26 hours. Because some ammonia was cracked thermally in the nitriding unit to hydrogen and nitrogen, the iron was incompletely nitrided. Based on a gain in weight of 2.78 pounds due to addition of nitrogen, the atom ratio of nitrogen to iron was calculated to be 0.36; this ratio was also obtained by chemical analysis:

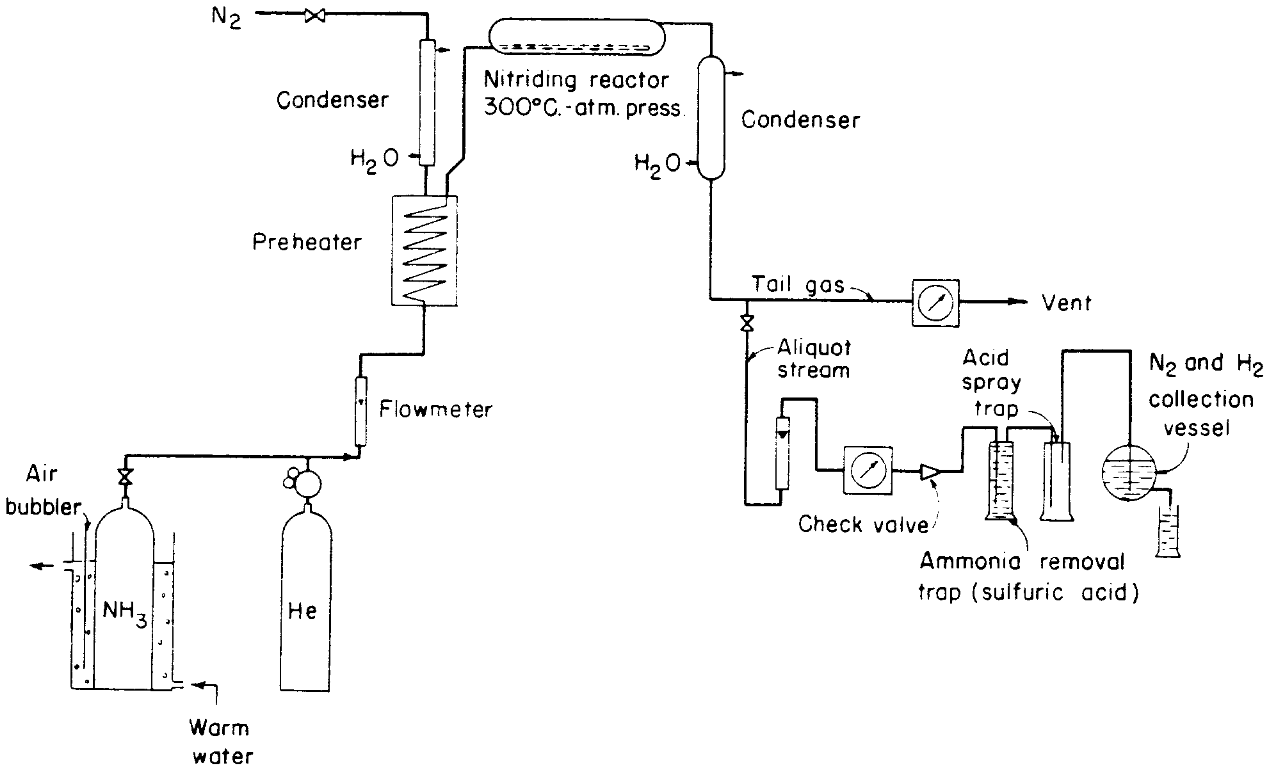

FIGURE 2. - Unit for Nitriding Reduced-Iron Catalyst for Fischer-Tropsch Synthesis.

	Weight-percent
Fe......................	83.6
N.......................	7.52

For complete nitriding to Fe_2N, the atom ratio would be 0.5.

Synthesis

A batch of 30.41 pounds (0.275 cubic foot) of nitrided catalyst was charged to the synthesis reactor to a height of 6 feet. The reactor was a 3-inch, schedule-80 steel pipe, 10 feet in length. Figure 3 shows a simplified flowsheet of the oil-circulation pilot plant. Recycle oil from a previous experiment with nitrided iron was used as the initial cooling medium. The catalyst was brought on stream and kept at 200° to 220° C. and 300 p.s.i.g. until a constant activity was obtained. Carbon dioxide was scrubbed from the exit gas with a 20-percent solution of monoethanolamine. At an oil-circulation rate of 2.5 g.p.m., the linear velocity of the oil was sufficient to expand the catalyst bed 10 to 20 percent from its original volume and thus prevent agglomeration.[11] The height of the bed was indicated by a weighted ball floating on the surface of the catalyst bed. A rod extending from the float to a gage glass above the reactor allowed visual observation of the bed height at all times. The

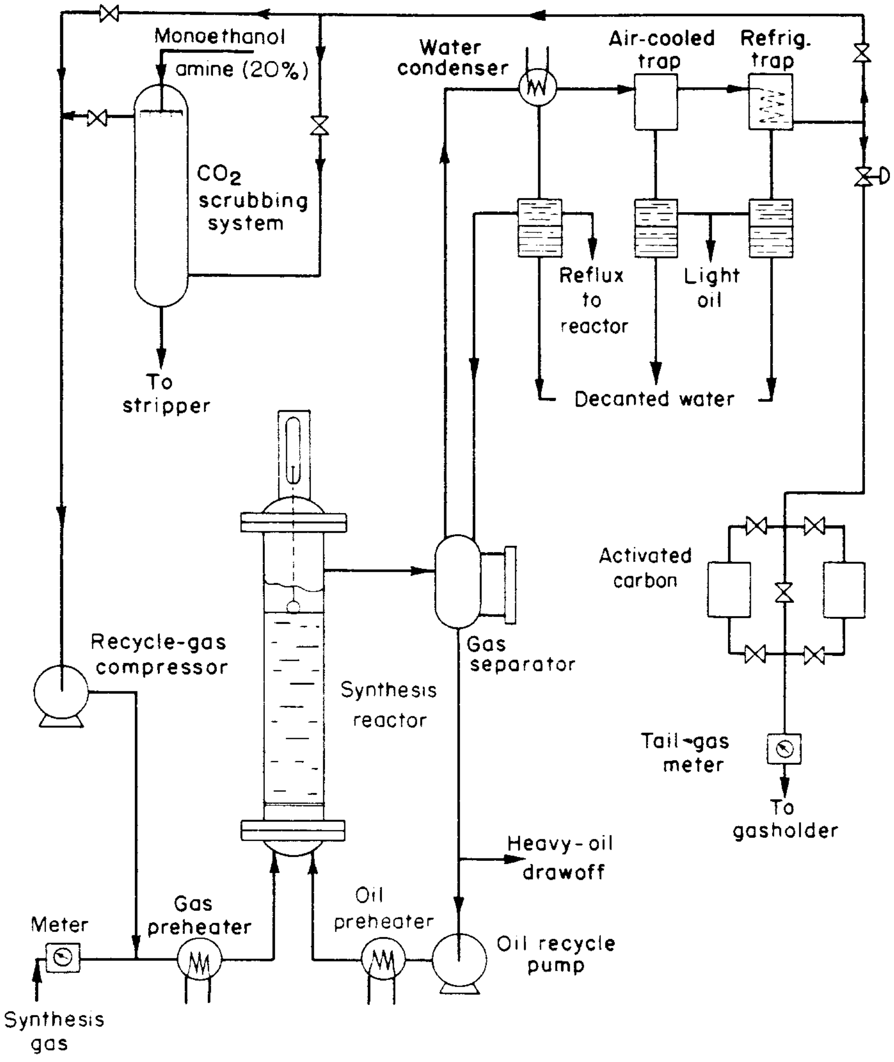

FIGURE 3. - Flow Diagram of Oil-Circulation Process for Fischer-Tropsch Synthesis.

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[11] Work cited in reference 10, p. 2.

exit gas, with carbon dioxide removed, was recycled from the start. Initially ammonia was displaced from the catalyst. To prevent deposition of solid ammonium carbonate from the cooled tail gas in the lines, the gas leaving the condenser was bubbled through water. This procedure was continued as long as ammonium carbonate was detected in the water.

Because the primary objective was to produce a gasoline with high alcohol content, experimental conditions were varied frequently to determine the effect upon yields of oxygenates, gasoline, and synthesis gas conversion. Operating variables investigated included, temperature, pressure, gas-recycle ratio, space velocity, synthesis-gas composition, and synthesis with and without reflux of oil to the reactor. These changes are shown in the chronological log of table 1. Synthesis was maintained at each set of conditions for several days until a steady state had been reached. When constant conditions were obtained, the products were recovered quantitatively. Operating and yield data for 20 steady-state periods are given in table 2. Although the catalyst was still fairly active, the experiment was voluntarily terminated at the end of 3,700 hours.

Processing and Evaluating Products

The following method was used to process and evaluate the product streams for the 20 steady-state periods shown in table 2. The product streams were collected over a 48-hour period. They were refrigerated to 5° C. for at least 24 hours, during which time a phase separation generally occurred. The oil phases from the light and heavy oil streams were combined and distilled into six fractions with boiling ranges of below 100° C., 100° to 150° C., 150° to 200° C., 200° to 250° C., 250° to 300° C., and above 300° C.

Distillation was begun at atmospheric pressure in a glass column packed with stainless steel helices and having an efficiency of 30 theoretical plates. When the pot temperature reached 300° C., the residue was removed and distilled in another unit under vacuum to prevent decomposition. Each oil fraction was analyzed for functional groups, esters (-COO), ketones (-CO), acids (-COOH), alcohols (-OH), terminal olefins (-CH=CH), internal olefins (-CH=CH-), and branched olefins (>C=CH) by infrared spectrometry. The amounts of alcohols and other oxygenates in each fraction were then estimated by assigning the molecular weights given in table 3 to the oxygenated compounds in each fraction.[12] These molecular weights were based upon the information reported previously by Anderson, Feldman, and Storch for a nitrided fused-iron catalyst.[13]

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[12] 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.

[13] 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.

TABLE 1. - Log of operating conditions for Fischer-Tropsch synthesis in oil-circulation pilot plant with nitrided fused-iron catalyst (Experiment 41)

Period....................				I[1]	II	III	IV	V	VI	VII	VIII	IX	X	XI
Catalyst age..........hours	0-10	10-18	18-106	106-205	205-373	373-488	488-911	911-1100	1100-1385	1385-1577	1577-1747	1747-1933	1933-2034	2034-2125
Space velocity.......vol./vol.-hr.	300	300	200	200	200	300	300	300	300	200	200	135	200	200
Maximum temperature..........°C.	75-200	212	212	220	230	240	240	240	240	230	220	210	210	210
Temperature differential.......°C.	1-2	2	2	1	2	3	3	3	3	3	2	2	2	3
Reactor pressure, inlet....p.s.i.g.	305	304	305	308	306	306	305	304	303	302	303	303	304	398
Pressure differential.......p.s.i.	7	7	8	10	8	8	8	6	8	8	8	8	8	5
Recycle to fresh gas ratio........	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0	1.0	1.0	1.0	1.0	1.0	1.0
CO_2 scrubbing..................	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes
Fresh gas ratio, H_2:CO..........	1.0	1.0	1.02	1.01	1.01-1.03	0.96	1.01-1.03	1.01-1.00	0.99-1.01	0.96-1.00	1.01-0.98	1.02-1.02	1.01-1.02	1.01-1.01
Usage ratio, H_2:CO..............	-	-	-	.69	.77- .82	.74	.83- .84	.69- .70	.82- .81	.71- .75	.75- .71	.72- .72	.76- .78	.75- .73
CO_2-free contraction.......percent	16.2	31.5	39.4-31.0	40.4-39.9	53.8-59.3	58.8-63.0	61.1-64.6	54.9-55.9	65.7-62.2	63.4-63.0	51.4-52.3	53.1-53.7	40.5-41.2	49.9-49.5
H_2 conversion..............do...	-	-	-	33.4	50.5-57.5	58.6	60.7-62.6	49.4-50.1	64.5-60.9	59.5-58.9	46.8-46.3	45.8-46.8	36.5-37.0	44.8-43.7
CO conversion..............do...	-	-	-	48.8	66.8-72.2	77.2	74.4-76.8	73.1-71.6	77.5-76.1	80.3-78.5	63.0-63.8	65.0-66.5	48.6-48.1	60.2-60.8
H_2+CO conversion..........do...	-	-	-	41.5	58.7-64.7	67.9	67.5-69.6	61.1-60.9	71.0-68.4	70.1-68.7	54.8-55.2	55.3-56.5	43.5-42.5	52.4-52.2
Reflux of oil...................	No	No	No	No	Yes	Yes	Yes	No	No	No	No	No	No	No

Period....................	XII		XIII				XIV	XV	XVI	XVII	XVIII	XIX	XX
Catalyst age..........hours	2125-2245	2245-2341	2341-2389	2389-2435	2435-2525	2525-2568	2568-2688	2688-2856	2856-3048	3048-3196	3196-3359	3359-3527	3527-3695
Space velocity.......vol./vol.-hr.	200	200-112	112	112-200-112	112	112-200	200	200	300	300	300	300	500
Maximum temperature..........°C.	200	200	200	200	200	200-220	220	220	240	240	240	240	260
Temperature differential.......°C.	3	3	3	3	3	3	2	2	2	2	2	2	4
Reactor pressure, inlet....p.s.i.g.	398	397	398	399	400	400	399	400	400	399	400	399	401
Pressure differential.......p.s.i.	5	5	4	6	6	6	5	5	5	5	6	6	8
Recycle to fresh gas ratio........	1.0	1.0	1.0	1.0-5.0	5.0	5.0-1.0	1.0	2.5	1.0	1.0	1.0	2.5	1.0
CO_2 scrubbing..................	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Fresh gas ratio, H_2:CO..........	1.00-1.01	1.03-1.01	1.00	1.0	1.0	1.0	1.00-1.01	0.97-1.00	0.99-1.01	0.99-0.99	0.71-0.68	0.67-0.68	0.68-0.66
Usage ratio, H_2:CO..............	.70- .79	.72- .67	.65	changing	1.09-1.11	changing	.75- .74	.88- .91	.76- .80	.76- .77	.69- .65	.67- .70	.64- .63
CO_2-free contraction.......percent	37.0-35.6	49.2-50.3	50.5	do.	54.6-51.4	do.	44.4-45.1	53.5-50.8	52.2-55.6	54.9-57.3	59.4-60.4	64.3-66.4	64.5-65.4
H_2 conversion..............do...	31.2-32.0	41.7-42.2	41.0	do.	58.1-54.9	do.	40.3-39.1	53.1-50.0	48.9-52.7	51.9-54.5	61.7-62.0	68.4-71.9	66.7-67.7
CO conversion..............do...	44.4-40.8	60.1-64.0	63.1	do.	53.3-49.1	do.	53.8-53.5	59.0-55.2	63.9-66.7	67.4-69.6	63.6-64.7	69.3-69.1	70.4-71.7
H_2+CO conversion..........do...	37.8-36.4	50.8-53.1	52.0	do.	55.7-52.0	do.	47.1-46.3	56.1-52.6	56.4-59.7	59.7-62.1	62.8-63.6	68.9-70.2	68.9-70.1
Reflux of oil...................	No	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes

[1] Roman numerals refer to corresponding columns in table 2.

TABLE 2. - Summary of steady-state conditions and yields from Fischer-Tropsch synthesis in oil-circulation pilot plant with nitrided fused-iron catalyst (Experiment 41)

Period	No reflux		Reflux						No reflux											
	I		II		III		IV		V		VI		VII		VIII		IX		X	
Catalyst age................hours	157-205		323-370		444-476		665-905		1049-1097		1337-1385		1529-1577		1649-1697		1885-1933		1981-2029	
Space velocity.......vol./vol.-hr.	200		200		302		301		300		300		200		200		136		201	
Maximum temperature...........°C.	220		230		240		240		240		240		230		220		210		210	
Temperature differential.......°C.	1		2		3		3		3		3		3		2		2		2	
Average reactor pressure..p.s.i.g.	303		302		303		301		301		299		299		299		300		300	
Recycle to fresh gas ratio........	1:1		1:1		1:1		1:1		0		1:1		1:1		1:1		1:1		1:1	
Fresh gas ratio, H_2:CO...........	1.00		1.03		0.94		1.01		1.00		1.01		1.00		1.00		1.02		1.02	
Usage ratio, H_2:CO...............	.68		.82		.78		.81		.70		.81		.75		.73		.72		.70	
CO_2-free contraction.......percent	39.9		59.3		62.0		63.2		55.9		62.2		63.0		51.9		53.7		41.2	
H_2 conversion...............do...	33.6		57.5		61.8		61.0		50.1		60.9		58.9		46.2		46.8		37.0	
CO conversion...............do...	49.8		72.2		75.0		75.9		71.6		76.1		78.5		63.5		66.5		48.1	
H_2+CO conversion............do...	41.7		64.7		68.6		68.4		60.9		68.4		68.7		54.8		56.5		42.5	
A_v, activity coefficient:																				
Based on contraction......$hour^{-1}$	132		161		181		186		152		181		178		189		200		204	
Based on conversion........do...	139		186		217		215		174		215		208		205		216		212	
Yield, gm./$m.^3$ H_2+CO converted:																				
CH_4...........................	27.6	44.5	30.8	53.1	34.4	59.4	33.5	61.1	31.7	57.8	34.3	59.3	32.4	57.1	24.4	49.9	22.5	44.8	19.9	42.2
C_2=...........................	6.4		5.0		4.0		3.8		5.1		5.4		3.7		8.1		7.9		7.1	
C_2...........................	10.5		17.3		21.0		23.8		21.0		19.6		21.0		17.4		14.4		15.2	
C_3=...........................	21.5	61.0	21.4	59.1	23.3	63.8	20.1	50.8	22.7	61.6	16.9	58.8	19.0	57.1	19.3	48.0	18.8	47.4	21.5	47.0
C_3...........................	10.9		8.4		9.6		10.2		9.9		14.2		11.6		7.0		6.2		8.2	
C_4=...........................	16.8		15.1		15.8		10.7		13.5		11.7		12.6		11.7		11.9		8.3	
C_4...........................	6.6		7.7		8.5		5.7		8.2		8.2		7.6		5.9		6.4		6.2	
C_5=...........................	5.2		6.5		6.6		2.6		7.3		5.8		6.3		3.5		3.3		2.1	
C_5...........................	-		-		-		1.1		-		2.0		-		.5		.6		.7	
C_6=...........................	-		-		-		.3		-		-		-		.1		.2		-	
C_6...........................	-		-		-		.1		-		-		-		-		-		-	
Oxygenates, oil phase..........	18.5		3.6		5.2		8.5		6.4		13.1		5.7		16.1		7.5		20.6	
Oxygenates, water phase.........	27.0		31.5		22.9		23.1		27.6		31.3		40.2		32.0		37.1		29.5	
Total oxygenates...............	45.5		35.1		28.1		31.6		34.0		44.4		45.9		48.1		44.6		50.1	
Unknown........................	2.4		2.5		.0		.1		2.0		-		2.9		1.4		1.8		1.2	
Hydrocarbons, condensed.........	36.1		20.5		36.5		47.1		25.4		21.3		32.1		57.6		44.9		51.1	
Total recovery................	189.5		170.3		187.8		190.7		180.8		183.8		195.1		205.0		183.5		191.6	
Theoretical hydrocarbon yield...	202.0		200.8		199.5		200.3		200.3		199.6		200.1		201.1		202.6		203.0	
Water..........................	21.4		32.2		39.2		33.9		6.7		30.2		16.1		20.2		10.3		27.2	
Carbon dioxide.................	550		519		489		496		539		498		527		524		523		488	
Oxygenates in C_3+ hydrocarbons plus oxygenates....weight-percent	33.0		32.1		21.9		24.5		29.3		35.0		35.4		31.9		33.5		34.3	
Product distribution:																				
C_3+ - 200° C..............do...	84.4		93.1		84.2		85.9		95.0		97.0		86.1		82.1		81.5		86.7	
200° - 300° C..............do...	5.6		2.6		6.4		6.2		1.6		2.8		4.1		4.3		2.8		2.6	
> 300° C..............do...	10.0		4.3		9.4		7.9		3.4		.2		9.8		13.6		15.7		10.7	
Recovery....................do...	98.4		99.0		97.3		99.1		95.4		98.1		98.5		98.9		95.8		97.7	

Period	No reflux												Reflux							
	XI		XII		XIII		XIV		XV		XVI		XVII		XVIII		XIX		XX	
Catalyst age................hours	2077-2125		2197-2245		2341-2389		2640-2688		2808-2856		3000-3048		3143-3191		3311-3359		3479-3527		3647-3695	
Space velocity.......vol./vol.-hr.	201		201		112		201		200		300		299		299		300		499	
Maximum temperature...........°C.	210		200		200		220		220		240		240		240		240		260	
Temperature differential.......°C.	3		3		3		2		2		2		2		2		2		4	
Average reactor pressure..p.s.i.g.	396		396		396		397		398		398		397		397		397		397	
Recycle to fresh gas ratio.......	1:1		1:1		1:1		1:1		2.5:1		1:1		1:1		1:1		2.5:1		1:1	
Fresh gas ratio, H_2:CO...........	1.01		1.01		1.00		1.01		1.00		1.01		.99		.68		.68		.66	
Usage ratio, H_2:CO..............	.73		.79		.65		.74		.91		.80		.77		.65		.70		.63	
CO_2-free contraction.......percent	49.5		35.6		50.5		45.1		50.8		55.6		57.3		60.4		66.4		65.4	
H_2 conversion...............do...	43.7		32.0		41.0		39.1		50.0		52.7		54.5		62.0		71.9		67.7	
CO conversion...............do...	60.8		40.8		63.1		53.5		55.2		66.7		69.6		64.7		69.1		71.7	
H_2+CO conversion............do...	52.2		36.4		52.0		46.3		52.6		59.7		62.1		63.6		70.2		70.1	
A_v, activity coefficient:																				
Based on contraction......hour^{-1}	263		256		228		156		183		151		158		172		202		160	
Based on conversion........do...	283		264		237		162		193		169		180		187		225		182	
Yield, gm./m.^{3} H_2+CO converted:																				
CH_4...........................	19.1		18.1		17.1		21.8		20.0		28.1		29.1		20.3		17.8		22.0	
C_2=...........................	8.8	38.1	8.5	40.3	9.2	35.2	7.4	40.8	6.9	39.5	4.3	51.3	4.2	52.1	5.9	39.4	4.7	34.0	5.6	40.7
C_2............................	10.2		13.7		8.9		11.6		12.6		18.9		18.8		13.2		11.5		13.1	
C_3=...........................	16.3		20.8		18.3		17.1		17.5		16.3		18.7		18.4		18.0		19.1	
C_3............................	9.9		13.9		9.4		9.0		10.3		8.9		9.5		6.6		7.5		5.4	
C_4=...........................	8.1		10.8		8.7		6.9		7.4		10.0		10.9		9.6		8.3		11.2	
C_4............................	3.4	39.6	4.5	52.8	4.2	44.3	2.8	38.4	3.8	41.1	6.8	44.5	7.5	47.3	5.8	42.0	4.9	39.4	6.8	47.0
C_5=...........................	1.6		2.0		2.3		1.6		1.6		2.2		.4		1.4		.4		4.4	
C_5............................	.3		.6		1.2		.8		.4		.2		.2		.1		.2		.1	
C_6=...........................	-		.2		.2		.2		.1		.1		.1		.1		.1		-	
C_6............................	-		-		-		-		-		-		-		-		-		-	
Oxygenates, oil phase..........	12.3		26.2		14.1		12.4		28.5		17.8		6.8		21.4		28.7		19.1	
Oxygenates, water phase.........	31.8		24.6		21.8		42.9		25.5		34.2		28.1		13.8		15.5		7.6	
Total oxygenates..............	44.1		50.8		35.9		55.3		54.0		52.0		34.9		35.2		44.2		26.7	
Unknown.......................	4.9		1.3		8.3		.9		2.6		.0		.2		.9		1.0		.0	
Hydrocarbons, condensed.........	47.1		55.5		46.3		44.6		42.1		40.0		46.4		71.6		77.7		72.5	
Total recovery.................	173.8		200.7		170.0		180.0		179.3		187.8		180.9		189.1		196.3		186.9	
Theoretical hydrocarbon yield...	203.5		202.5		203.7		202.8		202.9		201.0		200.9		203.3		203.4		203.1	
Water..........................	14.1		22.5		4.2		16.0		59.9		30.5		32.9		6.0		23.3		8.2	
Carbon dioxide.................	519		481		558		515		410		489		484		571		538		578	
Oxygenates in C_3+ hydrocarbons plus oxygenates....weight-percent	36.1		32.5		32.8		40.4		40.5		38.1		27.3		24.1		27.8		18.3	
Product distribution:																				
C_3+ - 200° C.............do...	85.8		82.2		77.1		85.5		91.2		94.5		85.7		69.5		73.1		78.5	
200° - 300° C.............do...	3.0		3.6		3.8		3.3		8.1		3.4		1.6		4.8		3.6		6.0	
> 300° C.............do...	11.2		14.2		19.1		11.2		.7		2.1		12.7		25.7		23.3		15.5	
Recovery...................do...	95.8		98.2		95.4		96.8		96.2		97.5		95.7		97.7		98.8		97.4	

TABLE 3. - Estimated molecular weights of oxygenates in Fischer-Tropsch oil fractions

	Boiling range, ° C.					
	<100	100-150	150-200	200-250	250-300	300+
Range of alcohols, carbon number............	1-4	4-7	6-9	9-11	11-13	13+
Molecular weight:						
Alcohols.................	60	98	125	146	180	230
Acids....................	71	110	137	160	205	250
Esters...................	69	108	135	155	190	239
Aldehydes or ketones......	59	96	123	144	178	228

Direct mass spectrometric analysis of product water and of the aqueous phase distilled from the light oil was not possible because of the presence of higher alcohols. The major peaks of alcohols between C_4 and C_8 have no distinguishing mass spectral characteristics from hydrocarbons. The alcohols were therefore converted to their trimethylsilyl ether derivatives whose major mass spectral peaks lend themselves readily to quantitative determination.[14] Alcohols as high as C_8 in these alcohol-water mixtures have been identified and measured by this method. These calculations were based on the assumption that only normal alcohols were present. Considerable concentrations of isomeric alcohols would result in smaller calculated amounts of alcohols than are actually present. However, there is evidence that only small amounts of isomeric alcohols were present.

Molecular weights of alcohols in the oil phase for two periods were calculated from the mass spectrometer analyses of the silyl ethers and are compared with the assigned values in table 4. Although the calculated values were somewhat lower than the assigned values, the total calculated yields of alcohols (including the oil and water phases) were nearly the same.

Because routine mass spectrometric analysis of hydrocarbons is limited to identifying C_6 hydrocarbons and lower, the heavier hydrocarbons were removed from the tail gas in periods I to VII by passing the gas through a cold trap of dry ice and acetone, and in periods VIII to XX by passing the gas through a trap of activated carbon. The oil obtained in both cases was analyzed by infrared spectrometry for functional groups. Water obtained from these recoveries was analyzed by mass spectrometry.

14/ Langer, S. H., Friedel, R. A., Wender, I., and Sharkey, A. G. Jr., A New Mass Spectrometric Method for Determining Alcohols and Water in Complex Mixtures: The Fischer-Tropsch Product: Anal. Chem., vol. 30, 1958, pp. 1353-1356.

TABLE 4. - Molecular weights and specific yields of alcohols in Fischer-Tropsch oil fractions

	Boiling range, ° C.					
	<100	100-150	150-200	200-250	250-300	300+
Molecular weight:						
Calculated from mass spectrometer data:						
Period XVI	57.7	86.1	111.4	(1/)	(1/)	(1/)
Period XVII	53.5	82.7	128.3	(1/)	(1/)	(1/)
Assigned2/	60	98	125	146	180	230

	Gm./m.^{3} H_2 + CO converted	
	From calculated molecular weights	From assigned molecular weights
Specific yields of total alcohols:		
Period XVI	43.4	45.9
Period XVII	29.8	30.2

1/ No alcohols indicated by mass spectrometer analysis.
2/ Work cited in reference 12, p. 6.

In addition to this general method of processing the products, a special procedure was used to separate and process the products from period IV (table 2) into gasoline, diesel oil, fuel oil, and wax. The manner of processing is shown in figure 4. Because of the small yields of diesel oil, fuel oil, and

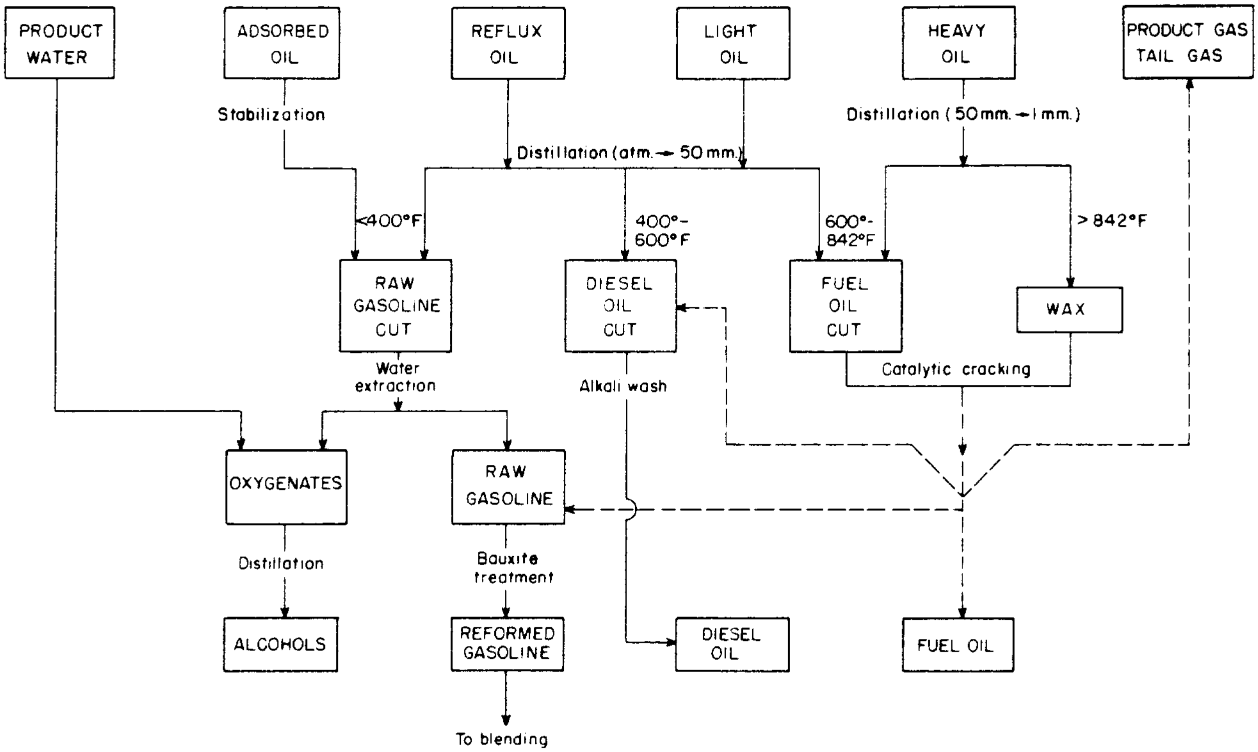

FIGURE 4. - Processing Product Streams in Fischer-Tropsch Synthesis Using Nitrided Fused-Iron Catalyst in Oil-Circulation Process.

wax, nothing was done to them after the initial distillation. The "raw gasoline cut" (excluding the oil adsorbed on the activated carbon, since the latter did not contain any alcohols) was extracted batchwise with water to remove water-soluble alcohols. Only the lower boiling alcohols are believed to contribute to the enhanced octane rating of the gasoline. After extraction the "raw gasoline" was reformed by bauxite treatment. If the water-soluble alcohols were not removed in the extraction, they would be decomposed by bauxite treatment. The conditions of this reforming were:

Catalyst..................................	Phillips Cyclocel
Temperature..........................°C.	390-400
Pressure........................p.s.i.g.	25
Liquid hourly space velocity...vol./vol.-hr.	1.5

This treatment will upgrade gasoline by removing hydroxyl and carboxyl groups, and by shifting the double bond from the alpha to an internal position. The resulting gasoline is referred to as "reformed gasoline" and was the base stock for blending with alcohols and polymer gasoline.

Alcohols present in the various water layers--"product water," extract from "raw gasoline cut," and condensate recovered after stripping the activated carbon traps with steam--were determined and are listed in table 5. A mixture of anhydrous alcohols--methyl, ethyl, and n-propyl--in the proportions synthesized was prepared for blending. No attempt was made to recover the original alcohols from the water layers.

TABLE 5. - Water-soluble alcohols recovered from Fischer-Tropsch synthesis in the oil-circulation pilot plant with nitrided fused-iron catalyst, period IV

	Water phase[1]			Water extract from "raw gasoline cut"			Total		
	Pounds per day	Gm./m.^{3} converted	Weight-percent	Pounds per day	Gm./m.^{3} converted	Weight-percent	Pounds per day	Gm./m.^{3} converted	Weight-percent
C_1OH...	0.197	2.33	11.2	0.027	0.32	9.6	0.224	2.65	11.0
C_2OH...	1.085	12.86	61.5	.079	.94	28.1	1.164	13.80	56.9
C_3OH...	.481	5.70	27.3	.175	2.07	62.3	.656	7.77	32.1
Total	1.763	20.80	100.0	0.281	3.33	100.0	2.044	24.22	100.0

[1] Total for "product water" and condensate from stripping activated carbon traps.

Polymer gasoline, comparable to what could be made from the propylene and butylene produced in the synthesis, was obtained from the Gulf Corporation Laboratories for blending with the reformed gasoline. The quantity of polymer added, based on yields obtained in industrial polymerization units, was equal to 85 percent of the propylene and 95 percent of the butylene produced in the synthesis. Normal butane was added to the blended gasoline to bring the Reid vapor pressure to 10 pounds per square inch. Sufficient butane is produced in the synthesis to satisfy this requirement.

Catalyst Composition

To follow the changes in catalyst composition, 10 to 15 grams of catalyst was removed each week from the top of the reactor for chemical and X-ray diffraction analyses. Sampling was accomplished without disrupting synthesis conditions by means of the catalyst sampler shown in figure 5. This device was threaded into a 2-inch gate valve located on top of the reactor. A magnet was lowered through the valve to the top of the catalyst bed and then withdrawn. The sample was removed from the reactor under an inert atmosphere and immediately stored under toluene.

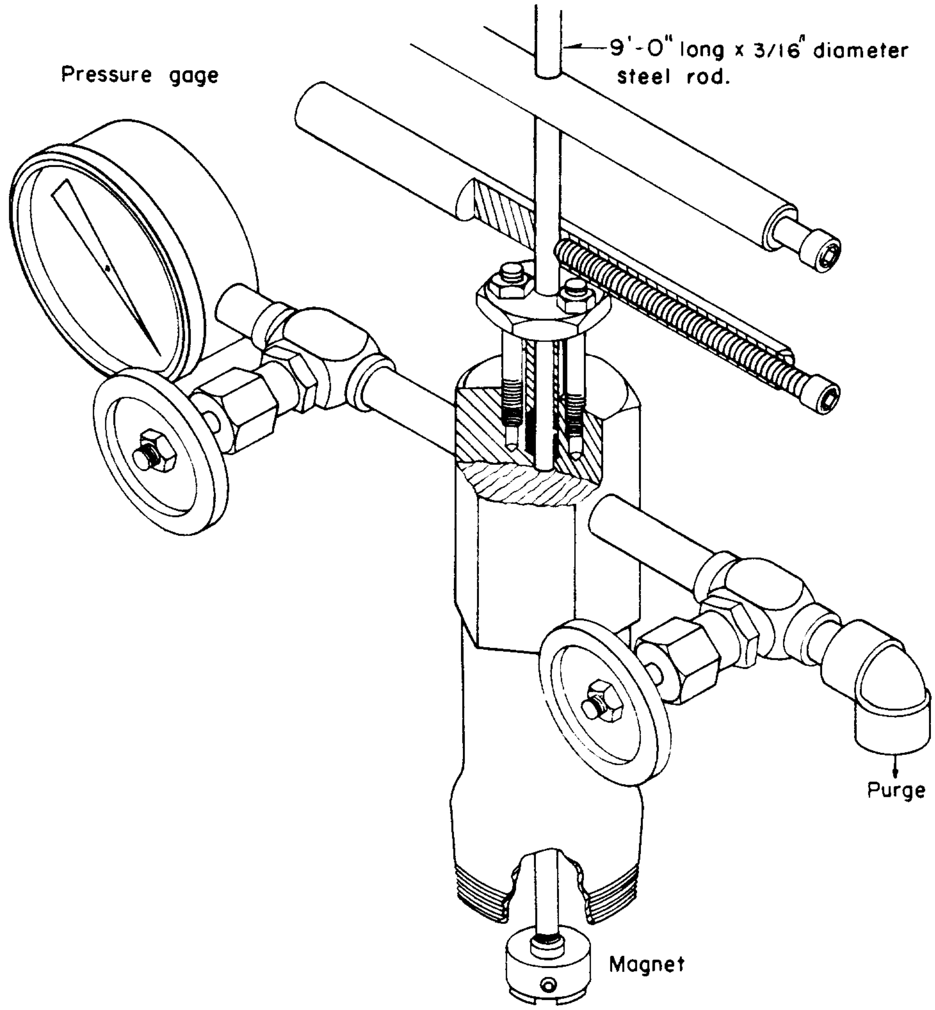

FIGURE 5. - Catalyst Sampler.

The catalyst was extracted with hot toluene and then analyzed chemically for total carbon, iron, and nitrogen. (Inerts (K_2O, MgO, SiO_2, and Cr_2O_3) were calculated on the assumption that the proportion of inerts to iron remained constant. Oxygen was determined by difference; hence the oxygen value is the least certain figure, as it contains the combined errors of the other determinations. A summary of the chemical and X-ray analyses is given in table 6.

TABLE 6. - Analyses of the nitrided fused-iron catalyst in the Fischer-Tropsch synthesis

State of catalyst and duration of synthesis	End of period	Chemical analysis, weight-percent				X-ray diffraction[1]
		Fe	N	C	Other	
Raw		67.27			0.28 (K)	Fe_3O_4
Reduced		90.4			.41 (K)	αFe
Nitrided		83.6	7.52		3.34 (Mg)	
Hours of synthesis:						
205	I		5.23	4.76		ϵFe_2X,[2] γFe_4X[2]
372	II	78.0	4.20	5.67		ϵFe_2X, γFe_4X
488	III	77.5	4.46	5.55		ϵFe_2X, evidence of γFe_4X, and questionable Fe_3O_4
576		77.6	3.55	5.95		ϵFe_2X, evidence of Fe_3O_4 and γFe_4X
745		77.4	3.49	6.57		ϵFe_2X
912	IV	77.1	3.53	6.84		ϵFe_2X, evidence of Fe_3O_4
1,080	V	76.3	3.36	7.08		ϵFe_2X, evidence of Fe_3O_4
1,244		76.6	2.96	7.39		ϵFe_2X, evidence of Fe_3O_4
1,415	VI	75.3	3.01	7.46		ϵFe_2X, evidence of Fe_3O_4
1,583	VII	76.5	3.27	7.67		ϵFe_2X, Fe_3O_4
1,751	VIII	75.7	3.03	7.76		ϵFe_2X, evidence of Fe_3O_4
1,915	IX	75.8	3.26	7.81		ϵFe_2X, evidence of Fe_3O_4
2,084	X	75.8	3.20	7.69		ϵFe_2X, evidence of Fe_3O_4
2,252	XII	73.2	2.32	6.77		ϵFe_2X, Fe_3O_4
2,417	XIII	71.9	2.10	6.50		ϵFe_2X, Fe_3O_4
2,575		71.2	1.43	6.67	0.34 (H)	ϵFe_2X, Fe_3O_4
2,741	XIV	70.9	1.73	6.83		ϵFe_2X, Fe_3O_4
2,900	XV	70.8	1.53	6.93		ϵFe_2X, Fe_3O_4
3,080	XVI	70.7	1.49	6.96		ϵFe_2X, Fe_3O_4
3,246	XVII	70.7	1.34	7.70		ϵFe_2X, Fe_3O_4
3,413	XVIII	70.3	1.37	7.55		ϵFe_2X, Fe_3O_4
3,581	XIX	71.3	1.37	7.40		ϵFe_2X, Fe_3O_4
Discharged catalyst		70.8	1.74	7.04	2.60 (Mg) <.01 (S)	ϵFe_2X, Fe_3O_4

[1] Listed in order of decreasing intensity of X-ray pattern.
[2] X denotes carbonitrides.

DISCUSSION OF RESULTS

Effect of Variables

Temperature

In the range 200° to 240° C. there was a slight effect of temperature on oxygenate production. Lower temperatures favored a higher oxygenate yield. Above 240° C. oxygenate production fell off more rapidly. This decline was observed in experiments in the slurry-type reactor.[15] Table 7 summarizes

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[15] Work cited in reference 12, p. 6.

several periods at constant space velocity and conversion. With increase in temperature, the yields of C_1 plus C_2 increased when $1H_2$:1CO synthesis gas was used. With $0.7H_2$:1CO feed gas not only was a lower yield of C_1 plus C_2 obtained, but the effect of temperature was reduced.

TABLE 7. - Effect of temperature on yields of oxygenates and C_1-C_2 from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

	Constant space velocity			Constant conversion			
Period..........................	VII	VIII	X	VI	VII	XX	XVIII
Temperature..................°C.	230	220	210	240	230	260	240
Space velocity.....vol./vol.-hr.	200	200	200	300	200	500	300
Reactor pressure........p.s.i.g.	300	300	300	300	300	400	400
Fresh gas, H_2:CO ratio..........	1	1	1	1	1	0.68	0.68
Reflux employed.................	No	No	No	No	No	Yes	Yes
Recycle to fresh gas ratio......	1	1	1	1	1	1	1
Synthesis-gas conversion..percent	68.7	54.8	42.5	68.4	68.7	70.1	63.6
Yield, gm./m.^{3} converted:							
C_1...........................	32.4	24.4	19.9	34.3	32.4	22.0	20.3
C_1 + C_2......................	57.1	49.9	42.2	59.3	57.1	40.7	39.4
Oxygenates......................	48.8	49.5	51.3	44.4	48.8	26.7	36.1

In general, nitrided fused iron produces lower molecular weight products--with the entire production shifted to lower boiling compounds--than a nonnitrided catalyst; thus the wax production is lowered while the yield of gaseous products is increased. The specific yield of C_1 plus C_2 at 240° C. for $1H_2$:1CO gas at 68.4 percent conversion and 300 p.s.i.g. pressure was approximately 60 grams per cubic meter of synthesis gas converted. For reduced fused iron at these same conditions, the yield was only 35 grams per cubic meter.[16] The nitrided catalyst was operated at an hourly space velocity of 300 vol./vol.-hr. and the reduced catalyst at 600 vol./vol.-hr. When $0.7H_2$:1CO gas was used at 400 p.s.i.g. and 240° C., the C_1 plus C_2 yield was 39 grams per cubic meter of synthesis gas converted for the nitrided catalyst as compared with 25 grams for a nonnitrided catalyst.

Pressure

Increasing the reactor pressure from 300 to 400 p.s.i.g. (compare periods X and XI, table 2) resulted in increased catalyst activity. The activity coefficient[17] based on synthesis-gas conversion, responded as the 1.08 power

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[16] Benson, H. E., Field, J. H., Bienstock, D., and Storch, H. H., Oil Circulation Process for Fischer-Tropsch Synthesis: Ind. Eng. Chem., vol. 46, 1954, pp. 2278-2285.

[17] Anderson, R. B., Seligman, B., Schultz, J. F., Kelly, R., and Elliott, M. A., Fischer-Tropsch Synthesis. Some Important Variables of the Synthesis on Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391-397.

of the absolute pressure $A_v \alpha P^{1.08}$. Hall, Gall, and Smith[18] found a linear relationship between pressure and conversion for pressures up to 675 p.s.i.g. With an ammonia-synthesis catalyst in the slurry process, they found that conversion was proportional to $P^{1.02}$; with a mill-scale catalyst in a fixed bed, conversion was proportional to $P^{1.00}$. Several days after the pressure had been increased from 300 to 400 p.s.i.g. in the experiment with a nitrided fused iron, the iron content in the recycle oil increased from its normal value of less than 0.01 weight-percent and varied between 0.03 and 0.3 weight-percent for the remainder of the experiment. The attrition of the catalyst in operation at 400 p.s.i.g. pressure, together with the loss due to removal of weekly catalyst samples, resulted in an overall loss of 29 percent of the original volume of catalyst charged. The decreasing A_v figures in table 2 seem to indicate reduction in catalyst activity. However, these values are based on the original charge of 0.275 cubic foot and are therefore lower than the true values. The activity of 182, reported for the final equilibrium period at the end of 3,700 hours, would be 257 if corrected to actual catalyst volume. As maximum activity of 283 was measured at the start of the 400-p.s.i.g. operation at 2,100 hours, loss in activity after 3,700 hours of synthesis was slight.

Increase in reactor pressure from 300 to 400 p.s.i.g. resulted in a decrease in the specific yields of C_1-plus-C_2 gas and an increase in production of oxygenates. Table 8 shows data for several periods at the same temperature and space velocity with and without reflux. Although the periods compared were nominally at the same space velocity based on the original volume of catalyst, the actual loss of catalyst from the reactor during the 400-p.s.i.g. periods was unknown.

TABLE 8. - Effect of reactor pressure on yields of oxygenates and C_1-C_2 from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

Period	VIII	XIV	VI	XVI	IV	XVII
Temperature °C.	200	200	240	240	240	240
Space velocity vol./vol.-hr.	200	[1] 200	300	[1] 300	300	[1] 300
Reactor pressure p.s.i.g.	300	400	300	400	300	400
Fresh gas, H_2:CO ratio	1	1	1	1	1	1
Reflux employed	No	No	No	No	Yes	Yes
Recycle to fresh gas ratio	1	1	1	1	1	1
Synthesis-gas conversion percent	54.8	46.3	68.4	59.7	68.4	62.1
Oxygenates yield gm./m.^{3} converted	49.5	56.2	44.4	52.0	31.7	35.1
C_1+C_2 yield gm./m.^{3} converted	49.9	40.8	59.3	51.3	61.1	52.1

[1] Space velocity actually higher due to loss of catalyst.

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[18] Hall, C. C., Gall, D., and Smith, S. L., A Comparison of the Fixed-Bed, Liquid-Phase ("Slurry"), and Fluidized-Bed Techniques in the Fischer-Tropsch Synthesis: Jour. Inst. Petrol., vol. 38, 1952, pp. 845-876.

Gas Recycle Ratio (Recycle to Fresh Gas)

Increasing the gas recycle rate should, by decreasing the residence time and by stripping the more volatile alcohols from the recycle oil, increase the oxygenate yield. At the termination of period XIII, the recycle rate was raised from 1:1 to 5:1. Because of this high gas flow, the liquid level could not be maintained in the reactor. However, the following changes, as noted in table 9, were observed: At the higher recycle rate the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, was retarded by decrease in the partial pressure of the water vapor. The specific yield of carbon dioxide was decreased from 558 to 296 grams per cubic meter converted, and the usage ratio was increased from 0.6 to 1.1. The oxygenate content of the oil was increased as well as the total oil production.

TABLE 9. - Effect of gas recycle, with and without reflux, on products from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

Period	XIII	A[1]	XIV	XV	XVIII	XIX
Temperature °C.	200	200	220	220	240	240
Space velocity vol./vol.-hr.	112	112	200	200	300	300
Reactor pressure p.s.i.g.	396	396	398	398	397	397
Fresh gas, H_2:CO ratio	1	1	1	1	0.68	0.68
Reflux employed	No	No	No	No	Yes	Yes
Recycle to fresh gas ratio	1	5	1	2.5	1	2.5
Synthesis gas conversion percent	52	54	46.3	52.6	63.6	70.2
Usage ratio, H_2:CO	0.65	1.11	0.74	0.91	0.65	0.70
Functional group analysis (infrared):						
Light oil:						
Hydroxyl (-OH) weight-percent	6.1	8.8				
Ketone (-CO) do.	1.8	2.8				
Ester (-COO) do.	2.0	2.3				
Acid (-COOH) do.	0.07	0.91				
Heavy oil:						
Hydroxyl (-OH) do.	.45	1.3				
Ketone (-CO) do.	.95	1.7				
Ester (-COO) do.	2.1	3.3				
Acid (-COOH) do.	-	-				
Yield, gm./$m.^3$ converted:						
C_1+C_2	35.2	32.4	40.8	39.5	39.4	34.0
CO_2	558	296	515	410	571	538
Oxygenates:						
Oil phase	14.1		12.4	28.5	21.4	28.7
Water phase	30.1		43.8	28.1	14.7	16.5
Total	44.2		56.2	56.6	36.1	45.2

[1] A - A non-steady state period.

In two other instances in which the gas recycle to fresh feed rate was increased from 1:1 to 2.5:1 (table 9), the effect on the composition of the oil phase was noticeable. When reflux oil was removed, production of oxygenates in the oil phase increased from 12.4 to 28.5 grams per cubic meter converted. However, the total yield of oxygenates remained constant at about 56 grams per cubic meter converted. When the reflux oil was returned to the converter, the oxygenate content of the oil phase increased from 21.4 to 28.7 grams per cubic meter converted. This latter change was accompanied by an increase in the total yield of oxygenated material from 36.1 to 45.2 grams per cubic meter of synthesis gas converted.

In another comparison between periods V and VI (table 2) in which reflux was removed, oxygenates in the oil phase increased from 6.4 to 13.1 grams per cubic meter converted in going from no recycle to 1:1 recycle. The total oxygenate yield also increased from 34.0 to 44.4 grams per cubic meter converted.

Space Velocity

The effect of space velocity should be similar to that achieved by increasing the recycle gas rate, namely, decreasing the residence time and stripping the more volatile alcohols from the reactor. Table 10 shows this effect. With increase in space velocity, the conversion decreased, and consequently the quantity of unreacted gas in the reactor increased. The oxygenate content in the oil phase, as well as the total oxygenate yield, increased with increasing space velocity.

TABLE 10. - Effect of space velocity on yield of oxygenates from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

Period	IX	X	XIII	XII
Temperature °C.	210	210	200	200
Space velocity vol./vol.-hr.	136	201	112	201
Reactor pressure p.s.i.g.	300	300	396	396
Fresh gas, H_2:CO ratio	1	1	1	1
Reflux employed	No	No	No	No
Recycle to fresh gas ratio	1	1	1	1
Synthesis gas conversion percent	56.5	42.5	52.0	36.4
Oxygenate yield, gm./m.^{3} converted:				
Oil phase	7.5	20.6	14.1	26.2
Water phase	38.9	29.5	30.1	25.9
Total	46.4	51.3	44.2	52.1

Synthesis Gas Composition

A $1H_2$:1CO synthesis gas was consumed at a usage ratio of 0.7 to 0.8 over the nitrided fused iron compared with 0.90 to 0.95 over a reduced fused iron at 220° to 240° C. and 1:1 gas recycle. A $0.7H_2$:1CO synthesis gas has been shown to produce lower specific yields of C_1 plus C_2 and correspondingly heavier products.[19] When $0.7H_2:1CO$ gas was used with this nitrided catalyst (starting with period XVIII), the gas was consumed in the same ratio as that of the feed. The yield of C_1 plus C_2 gas was reduced considerably at 240° C. and remained unchanged when the temperature was increased to 260° C. The total yield of oxygenates at 240° C., 1:1 recycle, and with reflux returned to the reactor was the same as that with $1H_2:1CO$ gas, as shown in table 11. The oxygenate content of the oil phase was considerably higher when $0.7H_2:1CO$ gas was used. No tests were conducted with $0.7H_2:1CO$ gas without reflux. When the temperature was raised from 240° to 260° C., the oxygenate yield dropped from 36.1 to 26.7 grams per cubic meter of synthesis gas converted. When the gas recycle rate was increased from 1:1 to 2.5:1, the oxygenate yield rose from 36.1 to 45.2 grams per cubic meter of synthesis gas converted.

TABLE 11. - Effect of synthesis-gas composition on yields of oxygenates and C_1-C_2 from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

Period	XVII	XVIII	XIX	XX
Temperature .... °C.	240	240	240	260
Space velocity .... vol./vol.-hr.	299	299	300	499
Reactor pressure .... p.s.i.g.	397	397	397	397
Fresh gas, H_2:CO ratio	0.99	0.68	0.68	0.66
Reflux employed	Yes	Yes	Yes	Yes
Recycle to fresh gas ratio	1	1	2.5	1
Synthesis gas conversion .... percent	62.1	63.6	70.2	70.1
Usage ratio, H_2:CO	.77	.65	.70	.63
Yield, gm./m.^{3} converted:				
C_1+C_2	52.1	39.4	34.0	40.7
Oxygenates:				
Oil phase	6.8	21.4	28.7	19.1
Water phase	28.3	14.7	16.5	7.6
Total	35.1	36.1	45.2	26.7

Reflux of Oil

The production of oxygenated compounds, especially those in the oil phase, was affected appreciably by reflux of condensate to the reactor (fig.3). The effluent gas leaving the reactor was sent to a water-cooled condenser. The condensate separated into two phases. The aqueous phase was removed to avoid oxidizing the catalyst, while the oil phase was either returned to the reactor as reflux or removed. Table 12 shows several periods in which only the reflux was varied. When the oil phase was returned to the reactor, the oxygenate yield dropped sharply. It is believed that, with sufficient residence time in the reactor, the alcohols undergo dehydration to olefins. This hypothesis was supported by functional-group analysis of the oils; those cuts rich in alcohol had a low olefin content, while those with little alcohol had a high olefin concentration. Dehydration of ethanol and higher alcohols is thermodynamically possible at synthesis temperature. The reverse reactions, hydration of olefins, are not possible.[20]

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[19] Work cited in reference 16, p. 15.

[20] Work cited in reference 6, p. 1.

TABLE 12. - Effect of reflux on yield of oxygenates from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

Period	IV	VI	II	VII	XVII	XVI
Temperature..........°C.	240	240	230	230	240	240
Space velocity..........vol./vol.-hr.	300	300	200	200	300	300
Reactor pressure..........p.s.i.g.	300	300	300	300	400	400
Fresh gas, H_2:CO ratio	1	1	1	1	1	1
Reflux employed	Yes	No	Yes	No	Yes	No
Recycle to fresh gas ratio	1	1	1	1	1	1
Synthesis gas conversion..........percent	68.4	68.4	64.7	68.7	62.1	59.7
Oxygenate yield,[1] gm./m.^{3}	31.7	44.4	37.6	48.8	35.1	52.0
Oil phase	8.5	13.1	3.6	5.7	6.8	17.8
Water phase	23.2	31.3	34.0	43.1	28.3	34.2

[1] The oxygenate yield in this and subsequent tables includes the unknown components in the water phase. The unknown percentage is quite small. It is predominantly oxygenate, namely esters, acids, and carbonyls, with possible small quantities of hydrocarbons. By grouping the unknown together with the oxygenates, the error introduced is slight. The specific yield of this unknown is given in table 3.

As shown in figure 6, although the specific yields of oxygenates were lower with reflux, the composition of the total oxygenated product from both water and oil phases was fairly constant--alcohols 85 to 92 weight-percent, aldehydes plus ketones 3 to 8, esters 1 to 6, acids less than 1 percent. However, the percentage of alcohols in the oil phase was reduced during periods in which reflux was employed. Figure 7 shows the effect of reflux on the composition of oxygenates in the oil phase. In period XVI without reflux, alcohols were 81.5 weight-percent of these oxygenates, but in the comparable period XVII, with reflux, they amounted to 55.9 weight-percent. In period VI without reflux, alcohols constituted 88.2 weight-percent of the oxygenates in the oil phase, while in comparable period IV, with reflux, they were only 71.7 weight-percent of the oxygenates.

From mass spectrometer analyses of silyl ether derivatives of alcohols in the oil fractions, as well as in the aqueous phases of periods XVI and XVII, the effect of reflux on the distribution of C_1 to C_{10} alcohols was determined as shown in figure 8. When reflux was employed (period XVII) the percentage of higher molecular weight alcohols was decreased considerably, indicating that these alcohols were dehydrated more readily than the lower molecular weight alcohols. Of the total alcohols produced in both periods, ethyl alcohol was predominant; the amount of alcohols decreased progressively from C_3 to C_{10} with increase of molecular weight.

Gasoline Processing

The final product distribution from period IV is shown in figure 9 and table 13. The "reformed gasoline" had a RON of 63.9 and an unusual susceptibility to TEL; 1 milliliter of TEL increased the octane number to 87.0. In another experiment the octane number of a reformed gasoline prepared from a reduced iron catalyst was increased only 9.6 points. The RON for the various gasolines and blends is given in table 14. For the blends, octane number is a linear function of alcohol content as shown in figure 10. The maximum amount of water-soluble alcohols synthesized in period IV amounted to 28.4 weight-percent of the finished gasoline. The finished gasoline did not include the small amount of C_5 and C_6 hydrocarbons in the tail gas. Thus, without addition of TEL, this gasoline could be employed as a blend with lower grade gasolines. With the addition of 1 milliliter of TEL the octane number was raised to 98.5, qualifying the gasoline as premium grade.

A survey by the Ethyl Corporation of gasoline quality in the United States for February 1958 gave the following results:[21] Premium-grade gasoline averaged a RON of 98.5 with 2.57 milliliters of TEL; regular-grade gasoline averaged 91.1 RON and 1.86 TEL. A comparison of the products with those obtained

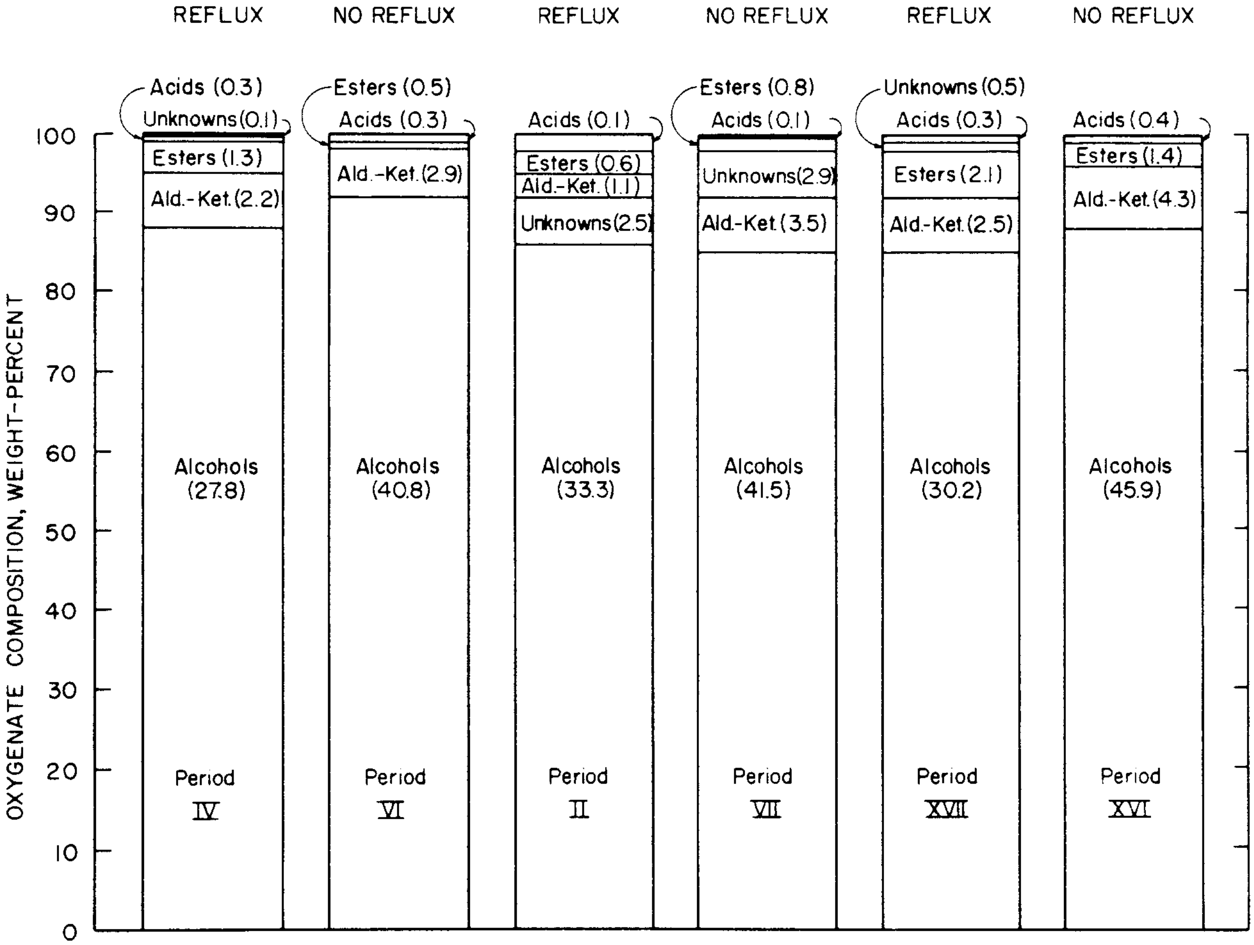

FIGURE 6. - Effect of Reflux on Composition of Total Oxygenates From Fischer-Tropsch Synthesis Using Nitrided Fused-Iron Catalyst in Oil-Circulation Process.

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[21] Oil and Gas Journal. Competition, Detroit Pushing Refiners: Vol. 56, No. 9, 1958, pp. 76-77.

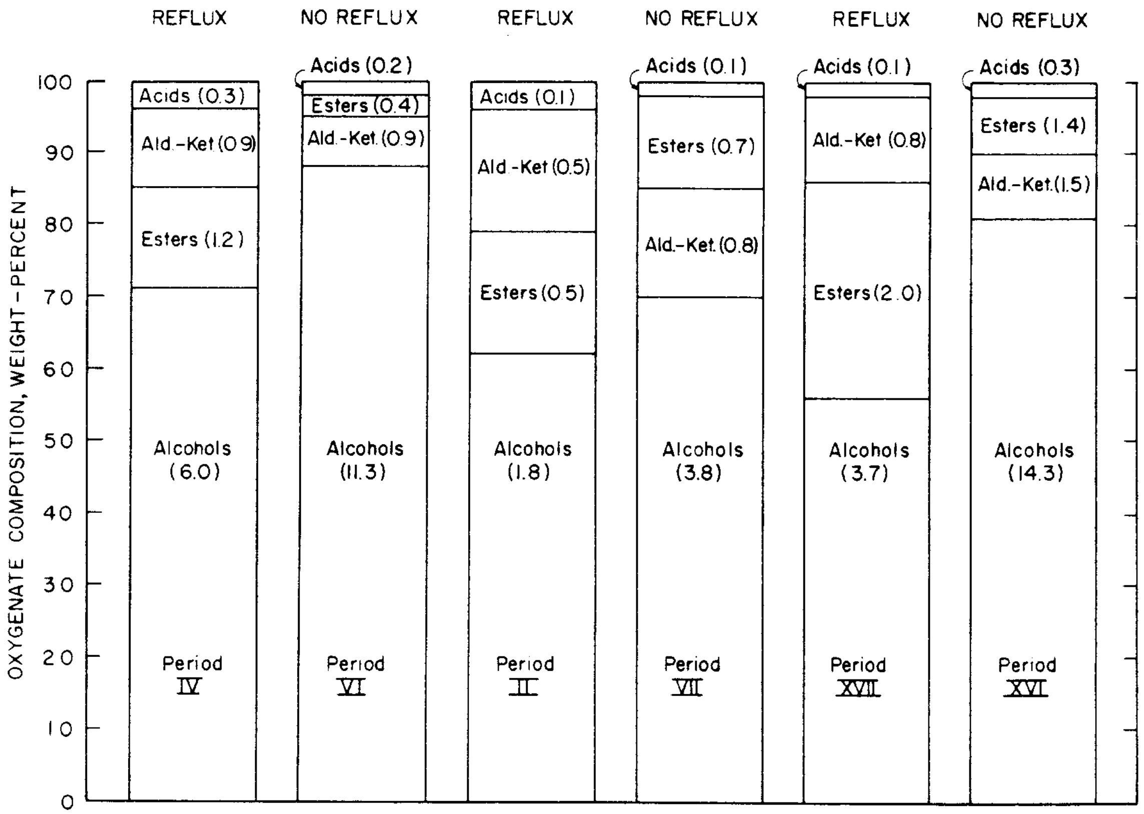
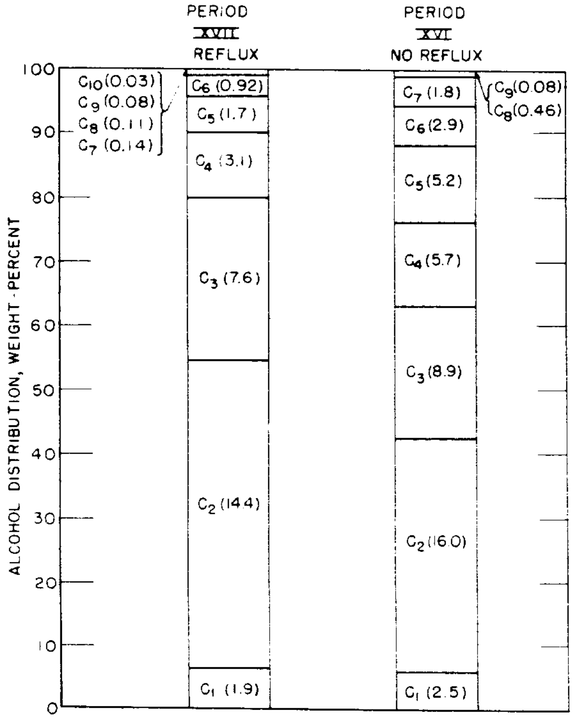


FIGURE 7. - Effect of Reflux on Composition of Oil-Phase Oxygenates From Fischer-Tropsch Synthesis Using Nitrided Fused-Iron Catalyst in Oil-Circulation Process.

FIGURE 8. - Effect of Reflux on Distribution of Alcohols From Fischer-Tropsch Synthesis Using Nitrided Fused-Iron Catalyst in Oil-Circulation Process.



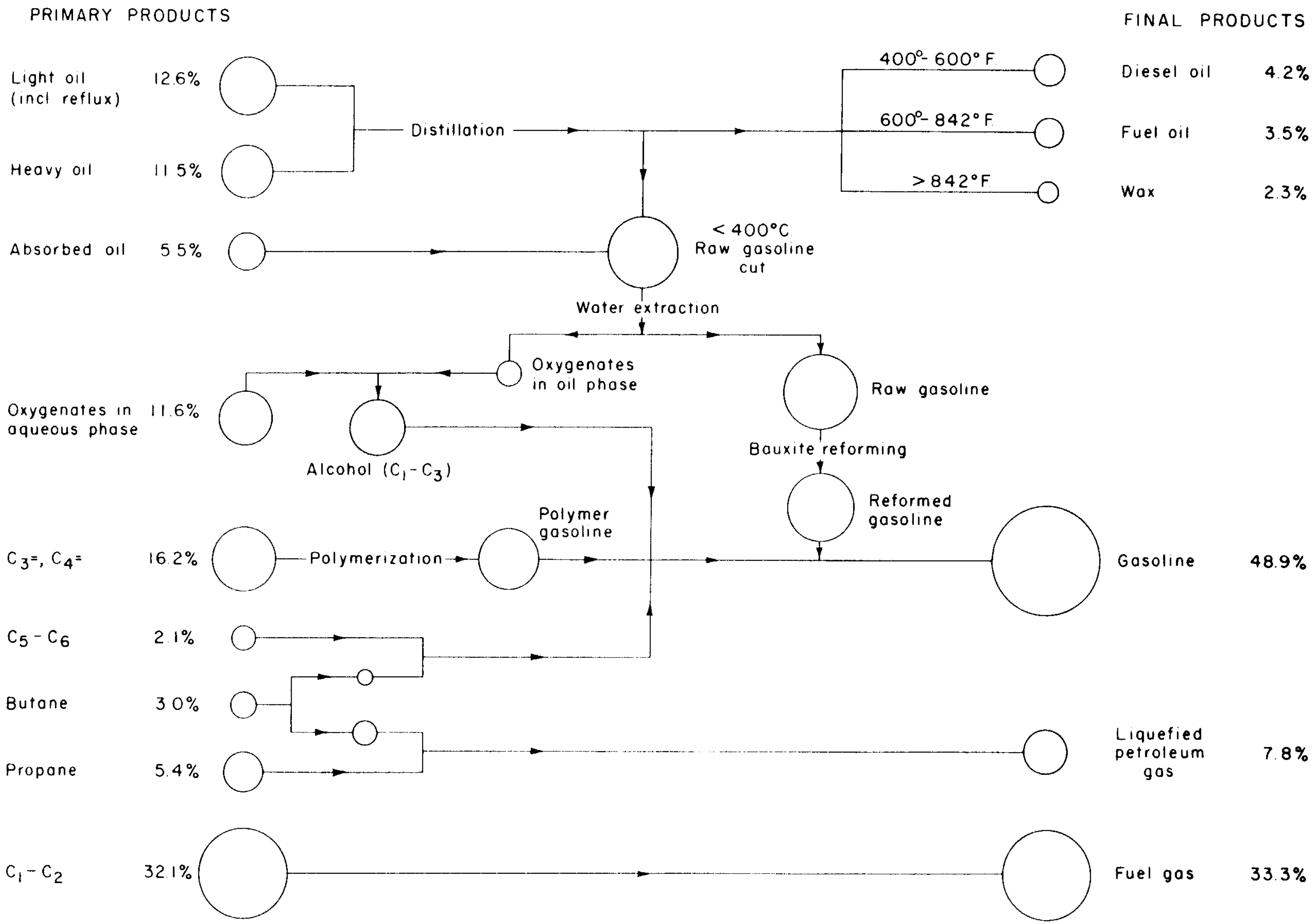


FIGURE 9. - Product Distribution From Fischer-Tropsch Synthesis Using Nitrided Fused-Iron Catalyst in Oil-Circulation Process.

from a reduced catalyst is shown in table 15. The nitrided catalyst, by shifting the product distribution to lower boiling compounds, gave a gasoline yield of 83 percent compared with 55 percent for the reduced iron.

TABLE 13. - Specific yields of products from Fischer-Tropsch synthesis with nitrided fused-iron catalyst, gm./m.^{3} converted gas, period IV after gasoline processing

C_1	33.5	61.1
$C_2=$	3.8	
C_2	23.8	
C_3	10.2	14.2
C_4	4.0	
Gasoline:		
C_4	1.7	89.5
C_5, $C_5=$	3.7	
C_6, $C_6=$	0.4	
Reformed	32.3	
Polymer	27.2	
Alcohols (C_1, C_2, C_3)	24.2	
Diesel oil	7.7	7.7
Fuel oil	6.3	6.3
Wax	4.2	4.2
Loss in bauxite reforming	0.8	7.3
Loss in polymerization of $C_3=$ and $C_4=$	3.6	
Extract not used in gasoline: C_4OH, ketones, unknown	2.9	
Total	-	190.3
Carbon dioxide	-	496
Water	-	34.2

TABLE 14. - Properties of gasoline from Fischer-Tropsch synthesis with nitrided fused-iron catalyst

	Reid vapor pressure, p.s.i.	RON		
		Clear	1 cc. TEL	3 cc. TEL
Raw gasoline cut	11.5	63.0		
Raw gasoline	12.0	56.4		
Reformed gasoline	12.8	63.9	87.0	
Polymer gasoline	3.0	94.8		
Reformed+Polymer+Butane	10.1	80.4	95.1	97.8
Reformed+Polymer+Butane+Alcohol (6.5 weight-percent)	10.2	83.2		
Reformed+Polymer+Butane+Alcohol (15.0 weight-percent)	10.2	87.2		
Reformed+Polymer+Butane+Alcohol (28.4 weight-percent)	10.1	92.9	98.5	

TABLE 15. - Final liquid-product distribution from Fischer-Tropsch synthesis with a nitrided fused-iron catalyst

Catalyst	Nitrided fused iron	Reduced fused iron
Synthesis conditions:		
Feed gas, H_2:CO	1	1.3
Temperature, °C.	240	235
Space velocity, vol./vol.-hr.	300	600
Synthesis gas conversion, percent	68.4	70
Reactor pressure, p.s.i.g.	300	300
Product distribution:		
Gasoline, <400° F, weight-percent	[1]82.9	[2]55.0
Diesel oil, 400°-600° F, do.	7.2	16.0
Fuel oil, 600°-842° F, do.	6.0	13.2
Wax, >842° F, do.	3.9	15.8
Total, do.	100.0	100.0
Composition of gasoline:[3]		
Polymer, do.	31.8	30.9
Reformed, do.	37.8	65.6
Alcohol, do.	28.4	-
Butane, do.	2.0	3.5
Total, do.	100.0	100.0
Reid vapor pressure, p.s.i.	10.1	9.9
Research octane number:		
Clear	92.9	84.8
Plus 1 ml. TEL	98.5	91.2

[1] Includes total C_1-C_3 alcohols produced.

[2] Alcohol yield low, not included.

[3] C_5, C_6 hydrocarbons in tail gas not included.

Catalyst Composition

Because the catalyst samples were taken from the top of the bed they may not be representative of the entire bed. Recycle oil leaving the top of the reactor is in contact with the highest concentration of oxidizing gases, water, and carbon dioxide, and the lowest concentration of reducing gases, hydrogen, and carbon monoxide. Recycle oil reentering the bottom of the reactor is at a maximum oxidizing potential; the synthesis gas as it enters is at a minimum oxidizing potential. However, gases that react on the catalyst surface probably first go into solution in the oil. As diffusion is relatively slow, it tends to average out the catalyst composition. This postulation is borne out by comparison of the compositions of discharged catalyst and of catalyst taken from the top of the bed in figures 11 and 12.

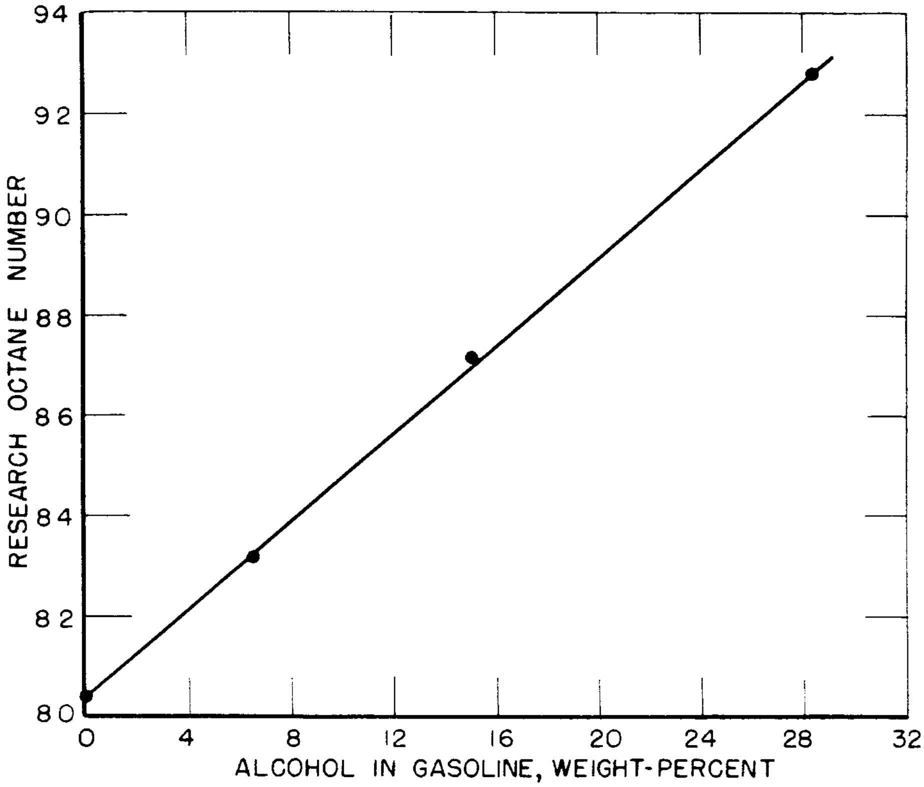


FIGURE 10. - Effect of Alcohol on Octane Number of Blended Fischer-Tropsch Gasoline.

A plot of the atom ratios of carbon, oxygen, and nitrogen referred to total iron is shown in figure 11. A plot of the percentage of iron in the form of magnetite, carbide, and nitride calculated from the chemical analysis is shown in figure 12. For computation ϵ-carbonitride was assumed to be a mixture of Fe_2N and Fe_2C.

In 2,000 hours of synthesis at 300-p.s.i.g. pressure, the nitrogen-iron atom ratio, N/Fe, decreased gradually from 0.36 and levelled out at 0.16; the C/Fe ratio increased gradually to 0.48, and the O/Fe ratio levelled out at 0.25. Of the total iron, 33 percent was present as Fe_2N, 49 percent as Fe_2C, and 18 percent as Fe_3O_4. Shultz and coworkers,[22] using the same type of catalyst (nitrided fused iron) in a fixed-bed reactor, reported the following distribution of iron after 2,000 hours operation at 100 p.s.i.g.: 60 percent Fe_2N, 30 percent Fe_2C, and 10 percent Fe_3O_4. At 300 p.s.i.g. they reported a greater rate of oxidation and carbon deposition; after 1,500 hours the distribution of iron in the various phases was 28 percent as Fe_2N, 45 percent as Fe_2C, and 27 percent as Fe_3O_4.

After the reactor pressure had been increased to 400 p.s.i.g., the catalyst composition changed drastically: The magnetite content increased considerably, and nitride and carbide decreased correspondingly. Distribution of iron in the various phases was then 16 percent as Fe_2N, 35 percent as Fe_2C, and 49 percent as Fe_3O_4. The atom ratio of O/Fe levelled out at 0.65, and N/Fe was 0.075. Even with this high magnetite and low nitride content, the activity and selectivity of the catalyst were not altered. If magnetite forms

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[22] Shultz, J. F., Seligman, B., Lecky, J., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis: Jour. Am. Chem. Soc., vol. 74, 1952, pp. 637-640.

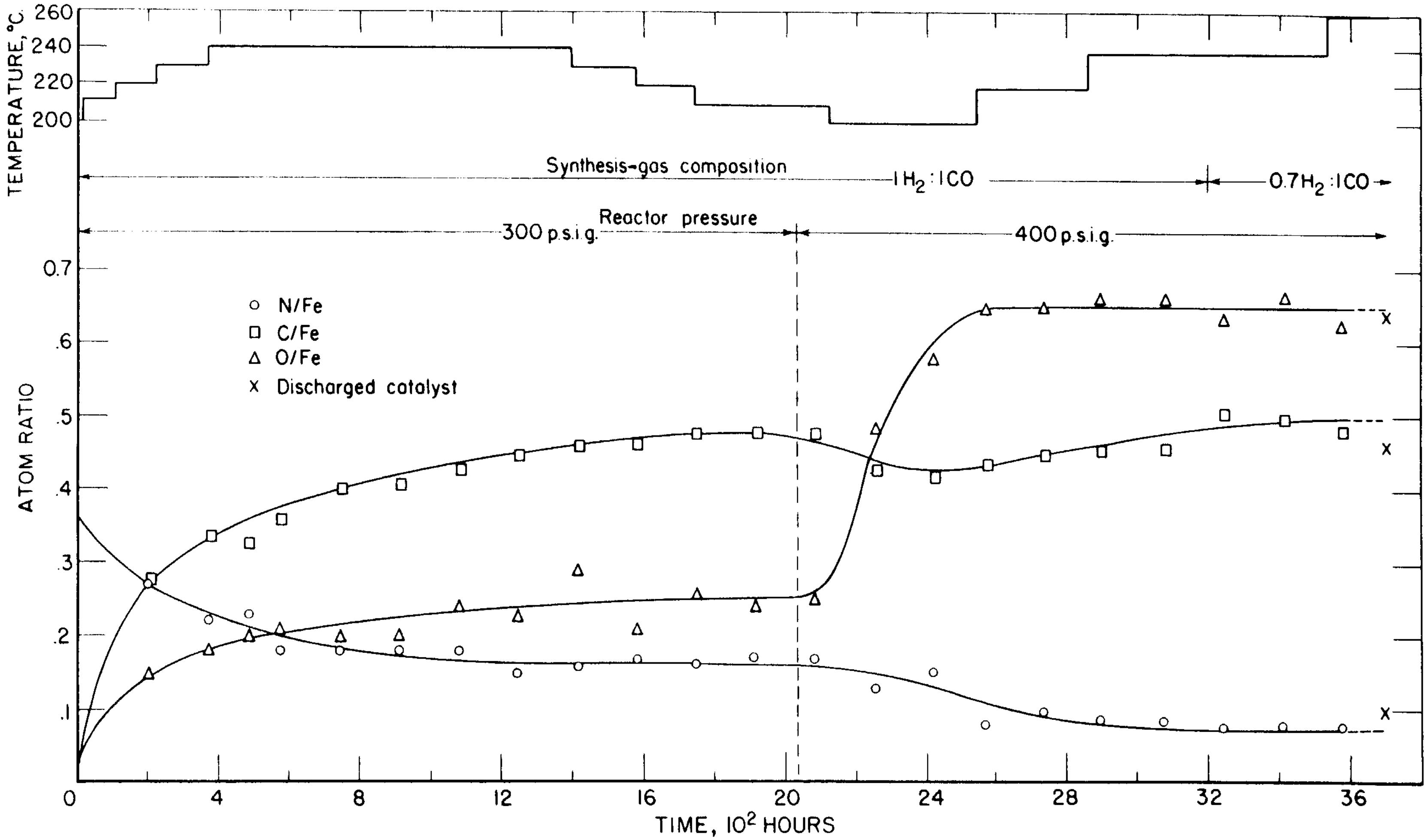

FIGURE 11. - Changes in Atom Ratios of Catalyst During Fischer-Tropsch Synthesis With Nitrided Fused-Iron Catalyst.

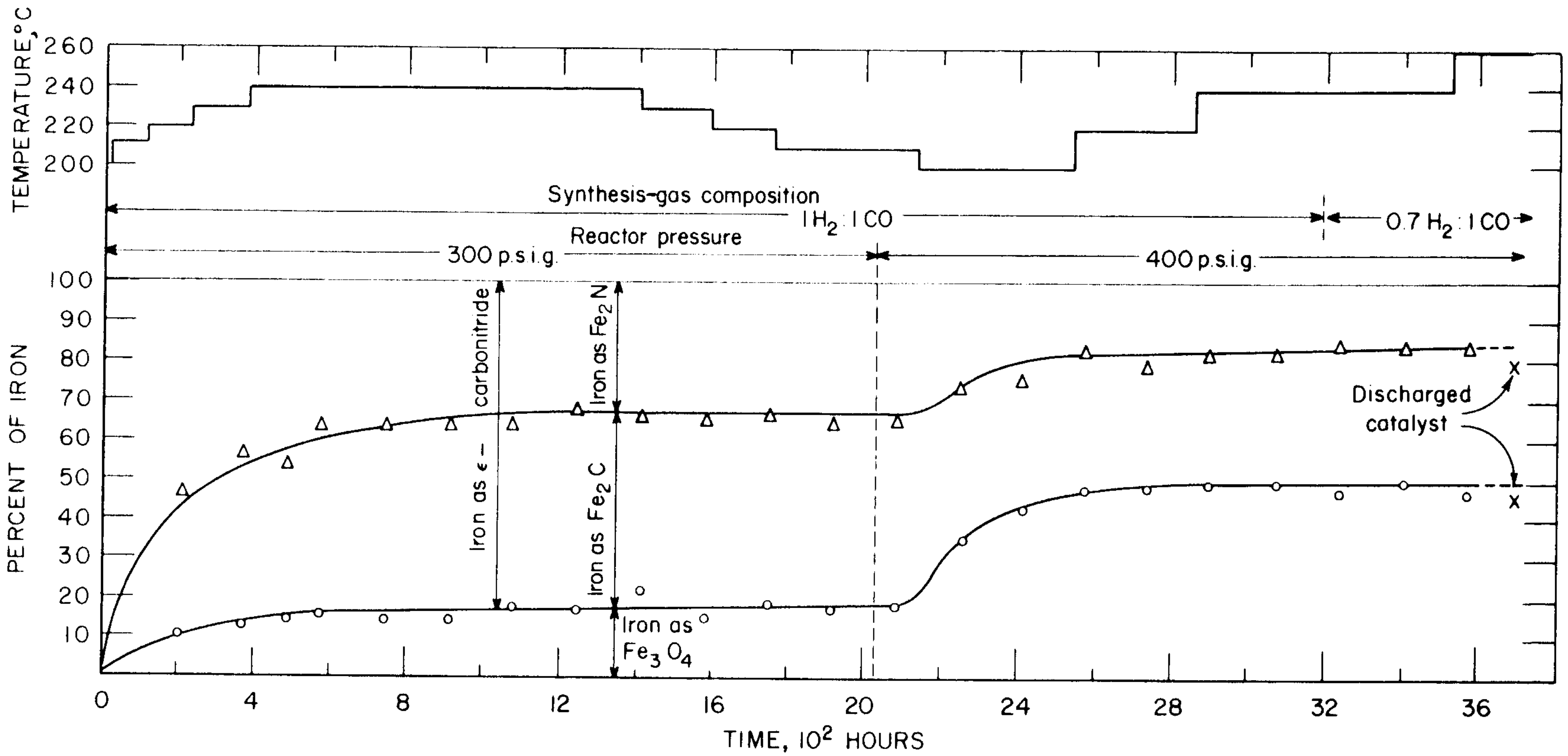

FIGURE 12. - Phase Changes of Catalyst During Fischer-Tropsch Synthesis With Nitrided Fused-Iron Catalyst.

at the core of the particle and grows toward the surface, there may be sufficient nitride at the surface to preserve the activity and selectivity of the catalyst. As a result of the rapid increase in magnetite content, however, the catalyst became softer, hydraulic attrition was more pronounced, and the iron content of the recycle oil increased at times from less than 0.01 to as high as 0.2 to 0.3 weight-percent. This attrition of the catalyst, together with the loss by removal of weekly samples, resulted in an overall loss of 29 percent of the original volume of catalyst charged.

CONCLUSIONS

Synthesis with a nitrided reduced magnetite was conducted in the oil-circulation pilot plant for a total of 3,700 hours without the need for catalyst reactivation. When the experiment was voluntarily terminated, the catalyst was still active. Previous experiments that had run for long periods with reduced iron catalysts had to be interrupted to reactivate the catalyst by reduction, or to discharge, reoxidize, and re-reduce the catalyst. Some of the longer previous experiments in the oil-circulation process were:

> Experiment 32 - 1/16-inch steel shot, 4,426 hours of operation, required five separate treatments of reoxidation and re-reduction. The maximum period of uninterrupted synthesis was 1,745 hours.
>
> Experiment 37 - 1,018 carbon-steel turnings, 2,700 hours of operation without interruption, 1,200 hours of which was above 290° C.

In the present experiment the catalyst was incompletely nitrided due to partial thermal cracking of ammonia in the nitriding unit. The nitrogen-iron ratio was only 0.36, while a value of 0.44 to 0.50 was desired. The activity of this catalyst was not as great as that of some reduced-magnetite catalysts. An activity coefficient (A_V) of 215 at 300 p.s.i.g. was obtained, compared with 314 for reduced magnetite operated with $1H_2$:1CO and 396 for reduced magnetite operated with $1.3H_2$:1CO.

Although the catalyst was not completely nitrided and its activity was lower than normal for fully nitrided iron, its selectivity was characteristic of nitrided iron. A product of lower average molecular weight than that from reduced iron was obtained. Yields of gasoline were substantially increased, while production of wax was reduced. At the same time gaseous (C_1 plus C_2) hydrocarbons were also produced in greater amounts. Substantially higher yields of oxygenates were formed, with total oxygenate yields reaching as much as 55 grams per cubic meter of synthesis gas converted. In comparison, oxygenate yields for reduced iron are only about 5 to 15 grams per cubic meter. Alcohols amounted to 90 percent of the oxygenates, and ethyl alcohol was predominant; the amount of each of the higher alcohols from C_3 to C_{10} decreased progressively with increasing molecular weight.

To determine optimum conditions for producing a gasoline rich in alcohol, the effect of a number of operating variables was investigated. These are summarized in table 16. Of the variables, reflux has the most effect. When reflux of oil to the reactor was eliminated, the total yield of oxygenates increased appreciably (30 to 46 percent), as did that of alcohols (25 to 52 percent). This effect can be explained by assuming that the longer the residence time of alcohols in the reactor, the more completely they undergo dehydration to olefins. Oil fractions rich in alcohol had a low olefin content, while those with little alcohol had a high olefin content. The fraction of higher molecular weight material in total alcohols was decreased when oil was refluxed to the reactor. Because complete elimination of reflux might result in too high a wax concentration in the oil for some conditions of operation, partial reflux, or a refluxing of oil from which the water-soluble oxygenates have been removed, may have to be employed industrially.

Increasing the pressure from 300 to 400 p.s.i.g. resulted in a decrease in the yield of C_1 plus C_2 by about 15 percent. The catalyst composition changed drastically; the magnetite content increased considerably, while the nitride and carbide content decreased. The activity of the catalyst was also immediately improved, with the activity coefficient responding as the 1.08 power of the absolute pressure. These improvements were offset, however, by a higher rate of attrition of the catalyst and a higher iron content of the recycle oil.

TABLE 16. - Effect of operating variables on composition of product from Fischer-Tropsch synthesis with a nitrided fused-iron catalyst

Variable	Range	Result
Temperature............°C.	200 to 240	Slight effect on oxygenate production (lower temperatures favor a higher yield). Increased yield of C_1+C_2 hydrocarbons.
Pressure..........p.s.i.g.	300 to 400	Increase in total production of oxygenates. Decrease in C_1+C_2 yield. Increase in catalyst activity.
Gas recycle ratio, recycle to fresh gas.	1:1 to 5:1	Increase in oxygenate content of oil phase. Increase in usage ratio. Decrease in yield of CO_2.
Fresh feed space velocity ....vol./vol.-hr.	100 to 200	Increase in total oxygenate production. Decrease in synthesis gas conversion.
Synthesis gas composition, H_2CO.	0.7 to 1:1	Decrease in oxygenate content of oil phase. No change in total oxygenate production. Increase in C_1+C_2 yield.
Reflux of oil.............	-	With reflux, total oxygenate yield drops sharply.

The effects of temperature on oxygenates were similar to those observed in slurry-type experiments with nitrided catalysts.[23] A reduction of the temperature from 240° to 200° C. resulted in an increase in the specific yield of oxygenates of about 6 to 8 grams per cubic meter of converted synthesis gas and, at the same time, a decrease in the specific yield of C_1 plus C_2 of about 18 to 20 grams per cubic meter of converted synthesis gas. While these changes are both desirable, operation at 200° C. would not appear feasible unless a much more active catalyst were employed; otherwise, a very small space-time yield of C_3+ material would be obtained. On the other hand, temperatures much above 240° C. would not be satisfactory. When the temperature was raised from 240° to 260° C. with $0.7H_2{:}1CO$, the specific yield of oxygenates decreased considerably.

Anticipated results of gas recycle were borne out well by tests conducted without recycle and with 1:1 and 2.5:1 gas recycle ratios. Because the more volatile oxygenates were stripped from the recycle oil at the higher gas recycle rates, the yield of oxygenates in the light-oil phase was increased. By decreasing the residence time of the alcohols in the reactor and thereby reducing the likelihood of dehydration, the higher gas-recycle rates also resulted in an increase in the total yield of oxygenates. Improved usage ratios (higher hydrogen consumptions) were obtained in all tests at the higher gas rates.

The effects of space velocity were similar to those described for gas recycle. By increasing the hourly space velocity the residence time of the alcohols in the reactor was reduced and the more volatile alcohols were stripped from the reactor. Consequently, the oxygenate content in the oil phase as well as the total oxygenate yield was increased. From a practical standpoint, space velocity would probably not be selected as a variable to improve the oxygenate yield. Increase of the fresh-feed-gas rate would also be accompanied by a decrease in conversion that would offset the gain in the oxygenate yield. To obtain sufficient conversion, several stages of synthesis would be required.

Although the total yield of oxygenates remained the same, the amount of oxygenates in the oil phase was considerably greater with $0.7H_2{:}1CO$ gas than with $1H_2{:}1CO$. As with reduced iron catalysts, $0.7H_2{:}1CO$ produced considerably less C_1 plus C_2 than did $1H_2{:}1CO$, the specific yields at 240° C. being 39.4 and 52.1 grams per cubic meter converted. This gas yield remained unchanged when the temperature was increased to 260° C. The carbon monoxide-rich gas was consumed in the same ratio in which it was fed. The $1H_2{:}1CO$ synthesis gas was consumed in a ratio of 0.7 to 0.8, compared with 0.90 to 0.95 at 220° to 240° C. for a 1:1 gas recycle ratio with reduced fused iron.

Primarily because the reflux oil was returned to the reactor, the oxygenate yield in period IV, from which the product streams were processed, was one of the lowest during the experiment. By shifting the product distribution to lower boiling compounds, the nitrided iron catalyst yielded 82.9 weight-percent gasoline for this period, compared with only 55 weight-percent for a reduced iron catalyst at about the same temperature.

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[23] Work cited in reference 12, p. 6.

A blended gasoline containing 28.4 weight-percent of water-soluble alcohols (methyl, ethyl, and n-propyl), in the proportion in which they were synthesized, had a RON of 92.9. With the addition of only 1 milliliter of TEL, a premium grade of gasoline with an octane number of 98.5 was obtained.

The susceptibility of the reformed gasoline to TEL was exceptional. One milliliter of TEL increased the RON from 63.9 to 87.0. The octane number of a reformed gasoline prepared from a reduced catalyst was increased only 9.6 points by the same amount of TEL.

A linear relationship was established between the alcohol content of the finished gasoline and octane rating for concentrations of alcohol ranging between 0 to 28.4 weight-percent. At the latter concentration the octane number was increased from 80.4 to 92.9.