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APPENDIX.—SYNTHESIS TESTS ON IRON CATALYSTS AT PRESSURES UP TO 103 ATMOSPHERES

by

S. Friedman[1] and M. D. Schlesinger[1]

The testing units of the Bureau's Catalysis and Physical Chemistry Section contained some components with maximum operating pressures of about 35 atmospheres. Therefore, tests at higher pressures were made by the Coal Hydrogenation Section in a system designed for operating with pressures up to 140 atmospheres. The reactor was a ¾-inch, schedule 80 type 316 stainless steel pipe (inside diameter 1.88 cm), surrounded by a boiling Dowtherm bath. Synthesis gas from a standard gas cylinder passed through a needle valve to regulate gas flow and through the orifice of a ring balance-type flowmeter, before entering the reactor. The gas stream from the reactor passed through a room-temperature trap, a cooled receiver, and through a back-pressure regulator that released the pressure to atmospheric. Carbon dioxide was removed from the product gas by a caustic scrubber, and the gas was then passed through a wet test meter to measure the output flow. Fifty cubic centimeters of catalyst were used in all of these tests. In most of these tests the temperature was held constant and the space velocity was adjusted to maintain the apparent CO_2-free contraction at about 65 percent.

Two fused iron catalysts were used in these tests: D3001 which is described on page 5, and D3008, which contained in the raw state 69.8 weight-percent Fe; 1.76, Al_2O_3; 1.05, K_2O; 0.34, TiO_2; and 0.12, SiO_2.

In preliminary experiments attempts were made to use nitrided catalysts directly in the synthesis, but severe operating conditions were encountered early in the test with plugging of small diameter tubing by solid ammonium carbonate which is formed from ammonia produced in the initial period of synthesis.

In the first experiment reported (table A–1), this problem was avoided by using a nitrided catalyst that had been operated in the synthesis with $1H_2+1CO$ gas for 40 days at 21.4 atmospheres and 225° to 240° C, in a standard catalyst testing unit (test X349) (*55*).[2] The second nitrided catalyst (D3008, table A–2) was reduced in H_2 at an hourly space velocity of 2,500 for 22 hours at 540° to 550° C, and nitrided in ammonia

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[2] Italicized numbers in parentheses refer to items in the bibliography preceding the appendix.

TABLE A–1.—*Fischer-Tropsch synthesis on nitrided iron catalyst D3001 at high pressures*

[$1H_2+1CO$ feed gas, 6- to 8-mesh catalysts from 21.4 atm, test X349]

Duration of test, hours	92	141	232	88	42
Operating conditions:					
Pressure, atm (absolute)	21.4	35	68	103	21.4
Temperature, ° C	259	258	259	259	259
Hourly space velocity	300	371	695	760	265
Conversion of H_2+CO, percent	63.2	67.8	63.6	66.5	66.7
Usage ratio, H_2/CO	.77	.75	.74	.76	.71
Carbon balance, weight-percent	97.0	99.5	97.5	98.0	98.9
Products, g/m³:					
CH_4	22.8	22.3	17.2	15.4	22.5
C_2	10.5	13.9	14.6	12.0	16.1
C_3–C_6 in gas	44.0	41.7	39.3	30.6	39.5
Oil boiling <200° C	22.6	54.7	54.3	62.5	48.7
Oil boiling 200°–350° C	11.9	18.7	22.4	24.8	19.9
Oil boiling >350° C	1.0	1.3	3.6	4.8	5.3
C_3^+	79.5	116.4	119.6	122.7	113.4
CO_2	326	345	314	311	325
Analysis of liquid fractions:					
<200° C:					
Infrared determinations:					
OH, weight-percent	11.3	12.3	9.7	10.4	12.2
CO, do	2.7	3.2	7.1	11.0	8.3
Bromine number	22	17	33	27	25
200°–350° C:					
Infrared determinations:					
OH, weight-percent	2.6	2.0	2.6	2.6	3.3
CO, do	1.9	1.6	7.2	8.6	8.0
Bromine number	23	19	20	12	28
>350° C:					
Infrared determinations:					
OH, weight-percent	----	.5	----	.5	.4
CO, do	----	.5	----	1.1	.2
Bromine number	----	17	----	23	32

at an hourly space velocity of 1,000 for 6.5 hours at 390° to 400° C. The nitrided catalyst was then treated with $2H_2+1CO$ gas at an hourly space velocity of 2,000 and atmospheric pressure for 1 hour at 145° C and 20 hours at 200° C. This treatment converted the ϵ-iron nitride to ϵ-iron carbonitride and removed most of the nitrogen that would be evolved as ammonia in the first few hours of the synthesis tests. In the third test (table A–3), 6- to 8-mesh reduced iron catalyst D3001 was used, after reduction in H_2 at 500° C.

TABLE A–2.—*Fischer-Tropsch synthesis with nitrided iron catalyst D3008 at high pressures*

[8- to 14-mesh catalyst with $1H_2+1CO$ gas]

Duration of test, hours	119	96	119	141	298	137	143	141	72
Operating conditions:									
Pressure, atm (absolute)	35	68	35	68	103	35	68	103	35
Temperature, ° C	208	207	226	226	226–236	242	242	242	242
Hourly space velocity	206	253	169	294	354	172	317	411	172
Conversion of H_2+CO, percent	55.9	51.3	59.2	59.4	58.4	59.3	58.9	60.3	59.7
Usage ratio, H_2/CO	.71	.82	.66	.70	.77	.72	.74	.75	.73
Products, g/m³:									
CH_4	9.0	7.4	10.1	18.9	8.9	13.3	11.8	11.2	12.2
C_2	9.2	7.6	7.6	9.4	8.1	8.8	9.1	9.4	10.6
C_3–C_6 in gas	31.7	24.4	24.5	25.2	23.1	26.8	24.1	25.8	28.0
Oil boiling, <200° C	39.7	43.8	50.4	55.9	57.3	53.2	53.9	59.7	45.2
Oil boiling, 200°–350° C	22.3	41.7	33.0	35.8	30.5	20.0	27.2	26.8	17.7
Oil boiling, >350° C	2.8	4.9	4.0	4.4	4.0	4.0	3.2	2.6	7.4
C_3^+	96.3	114.8	111.9	121.3	114.9	104.0	108.4	114.9	98.3
CO_2	280	209	345	303	293	331	321	309	345

TABLE A–3.—*Fischer-Tropsch synthesis with reduced iron catalyst D3001 at high pressures*

[6- to 8-mesh catalyst with $1H_2+1CO$ gas]

Duration of test, hours	167	329	135	143	236	47
Operating conditions:						
Pressure, atm (absolute)	35	68	68	68	68	68
Temperature, ° C	259	271	284	259	275	266
Hourly space velocity	180	278	551	278	415	285
Conversion of H_2+CO, percent	60.7	62.1	63.2	57.3	60.8	61.6
Usage ratio, H_2/CO	.72	.80	.72	.75	.72	.71
Products, g/m³:						
CH_4	10.9	10.2	12.1	7.1	9.9	8.9
C_2	13.2	10.5	12.3	7.9	9.7	8.7
C_3–C_6 in gas	32.6	28.0	34.2	24.3	24.1	23.3
Oil boiling, <200° C	35.7	48.2	36.3	40.2	42.4	40.0
Oil boiling, 200°–350° C	44.6	31.7	38.1	48.8	41.2	49.3
Oil boiling, >350° C	2.8	4.4	1.9	3.8	3.1	3.5
C_3^+	115.7	112.3	110.5	117.1	110.8	116.1
CO_2	288	300	330	266	318	322

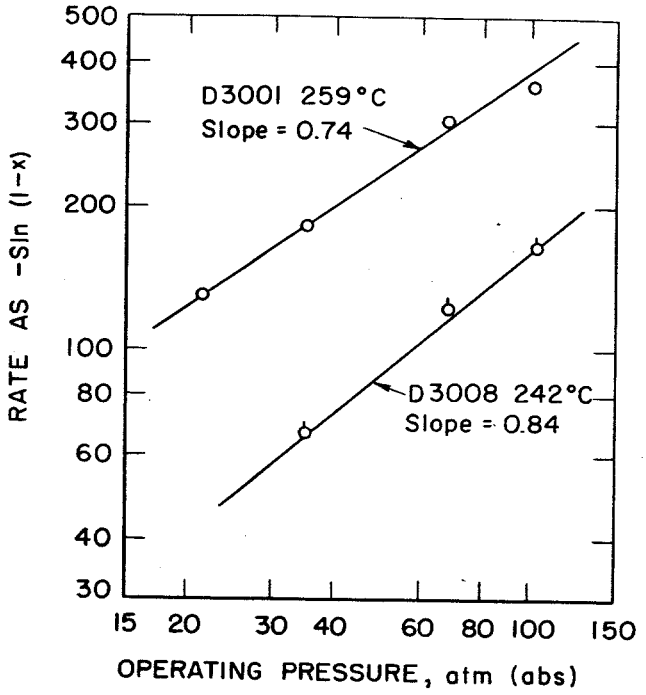

FIGURE 34.—Log-Log Plots of Pressure Dependence of Synthesis on Nitrided Iron Catalysts at High Pressure.

The activity decreased in first 2 weeks of synthesis but then remained essentially constant for as long as 48 days. The present data suggest that operating pressures up to 103 atmospheres does not decrease the life of the catalyst. The pressure dependence of synthesis is shown in figure 34, in which the quantity, $S\ ln\ 1/(1-x)$, where S is space velocity and x conversion of H_2+CO, is used as a measure of rate for tests at the same temperature. The rate increased with pressure to the 0.74 to 0.84 power for nitrided catalysts, and 0.52 for fragmentary data for reduced catalysts.

The selectivity for a nitrided catalyst as a function of pressure is shown in figure 35. In the pressure range 21.4 to 103 atmospheres, the yield of gaseous hydrocarbons decreased and the liquid hydrocarbons increased as pressure increased. Infrared analyses of liquid distillation fractions (table A–1) showed no systematic changes in composition with increasing pressure, in particular the yield of alcohols (OH) did not increase. The data for the reduced catalyst (table A–3) also indicated a small decrease in gaseous hydrocarbons and small increase in liquid hydrocarbons as pressure was increased. Yields of waxes (>350° C) in table A–3 are smaller than found in tests of reduced catalyst D3001 at 7.8–21.4 atmospheres (*8*).

The results of this study indicate that synthesis was not adversely affected by pressures up to 103 atmospheres. The synthesis rate increased moderately and the selectivity improved slightly as the pressure was increased. However, from an economic standpoint the small improvements in rate and selectivity observed in synthesis at high pressures would be outweighed by the added cost of compression and high-pressure equipment.

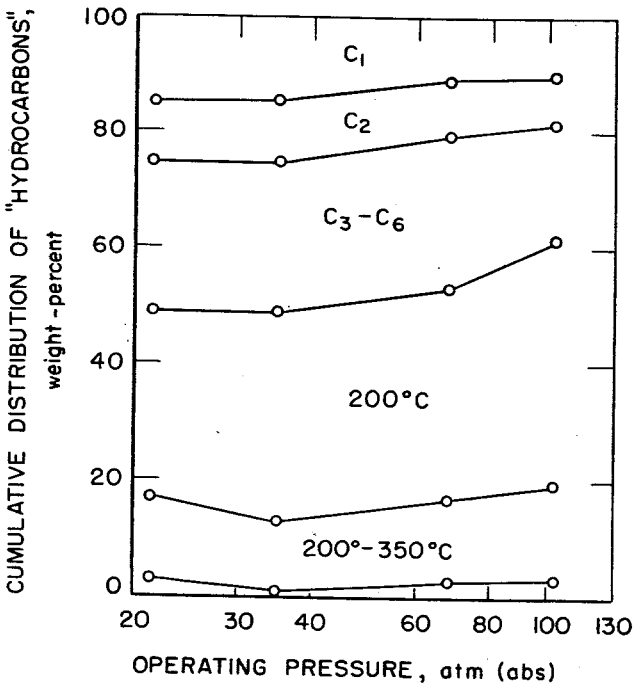

FIGURE 35.—Distribution of Hydrocarbons (Including Oxygenates Dissolved in Oil Phase) From Synthesis With Nitrided D3001 at High Pressures and 259° C Using $1H_2+1CO$ Gas.

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