liquid-nitrogen bath surrounding the trap was gradually lowered, and the escaping gases were collected in a 5-gallon sample vessel containing gas-saturated brine. Following removal of the gases, the hydrocarbons, which were liquid at 10° C., were collected in an ice-cooled trap and weighed, or measured, and the weight calculated from the specific gravity.

In some of the more recent tests (those having "X" before the test number), the vapors from the converters, after passage through the air-cooled and ice-cooled traps were led through a column of active charcoal in an 18-inch (length) by 2-inch (diameter) brass vessel. When iron catalysts were tested, carbon dioxide was removed before the gas entered the charcoal adsorber. The continuously collected sample of the exit gases from the charcoal adsorber and a sample of vapors periodically recovered from the charcoal by steaming were analyzed by use of a mass spectrometer. Seven-component mixtures containing H_2, CO, and C_1 to C_5 hydrocarbons could be analyzed with the desired accuracy. The liquid product recovered from the steaming of the charcoal was collected and weighed. This liquid product probably contained only little dissolved C_2 to C_4 hydrocarbons, whereas the liquid recovered by cooling to liquid-nitrogen temperatures and subsequent stabilization at 0° C. contained an appreciable quantity of these hydrocarbons.

The substitution of adsorption on charcoal for condensation at liquid-nitrogen temperatures and the independent instrumentation of each unit with geared needle valve and indicating flow meter for setting the feed gas rate, recording flow meter, back-pressure regulator, automatic pressure control on the liquid-vapor bath, combined with multiple-point temperature recorders, made it possible to operate these units with only two 8-hour shifts of three operators per shift.

SYNTHESIS-GAS MANUFACTURE

The gas used in the Fischer-Tropsch synthesis was manufactured at the Bureau of Mines in the water-gas generator previously described.[404] Natural gas, steam, and carbon dioxide were passed over a nickel catalyst at 1,000° C. to obtain the two gas mixtures ordinarily used in the synthesis, that is, $2H_2 + 1CO$ for cobalt catalysts and $1H_2 + 1CO$ for iron catalysts. The proportions of steam and carbon dioxide were varied to produce the desired hydrogen: carbon monoxide ratios. The synthesis gas contained 0.5 to 1.0 percent of methane and the same percentage of nitrogen, and less than 0.1 percent of carbon dioxide.

CONDITIONING PROCEDURES

All the catalysts as charged in the test converters were present in the form of oxides, oxide-hydrates, carbonates, or oxide-carbonate mixtures. Before use in the synthesis they were subjected to special conditioning treatment, which was usually a two-step procedure. The first step was the reduction of the catalyst. Using hydrogen at atmospheric pressure, two reduction procedures were employed. In the slow method, hydrogen was passed over the catalyst at a space velocity (volume of gas per hour per bulk volume of catalyst) of about 20 for about 24 hours. During the first 20 hours the temperature was gradually raised to a minimum of 360° C. and held at that point 4 hours longer. In the very early experiments before the conditions were standardized, reduction periods were sometimes 40 hours or longer, and temperatures sometimes rose as high as 370° C. Most of the iron catalysts and half of those in the cobalt group were reduced by this slow procedure. The rest of the cobalt catalysts were reduced by a rapid procedure in which the catalyst was heated to 400° C. in an atmosphere of nitrogen. Hydrogen was then run in for 2 hours at a space velocity between 3,000 and 3,500.

After reduction, the catalysts were in a highly active state and produced large amounts of methane and minor amounts of higher hydrocarbons from hydrogen-carbon monoxide gas. An induction procedure was desirable to reduce the methane yield and increase that of normally liquid hydrocarbons. Induction was carried out with synthesis gas by one of three procedures, identified as the rapid, intermediate, and slow methods. The rapid method required a period of 10 hours at atmospheric pressure to bring the catalyst up to the final operating conditions. The induction was started at a temperature at which the contraction was not greater than 20 percent, and this temperature was maintained for 2 hours. This initial temperature was usually 160° C. for cobalt catalysts and 225° to 230° C. for iron catalysts. The temperature was increased to a value at which the contraction was 30 percent and held at that point for 2 hours. In this manner the contraction was permitted to increase by 10-percent increments to 60 percent or more. If, however, a temperature of 200° C. in the case of cobalt catalysts, or 260° C. in the case of iron catalysts, was reached with little or no contraction, no further temperature increases were made, and the catalyst was reported to be inactive.

In the intermediate induction procedure, the reaction was started at a temperature at which the contraction was not greater than 30 percent. The induction period was approximately 36 hours. During this time the contractions gradually increased to a conversion of 50–60 percent, or the temperature rose to 260° C. for iron catalysts or 200° C. for cobalt catalysts, whichever condition was reached first. Most of the inductions by this procedure were conducted at atmospheric pressure; however, in a few cases the pressure was 100 pounds per square inch.

The slow induction method, used primarily for cobalt catalysts, involved a rigid temperature schedule. Following reduction, the temperature in the converter was dropped to 150° C. and synthesis gas introduced at atmospheric pressure at a space velocity of 100 at NTP. After a half hour at 150° C., the temperature was increased gradually and uniformly so that at the end of another hour it was 175° C. After 48 hours at 175° C., the temperature was increased to 180° C. and maintained there for 24 hours, and then increased to that temperature (usually 185° C.) necessary to give 70-percent contraction. During operation, contraction was maintained at about 70 percent by increasing the temperature to a maximum of 200° C. This induction procedure is identified as the "slow method with temperature schedule." A modification of the slow method, using a contraction schedule, was used in some of the experiments with cobalt catalysts. After the synthesis gas was passed over the reduced

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[404] Storch, H. H., Hirst, L. L., Fischer, C. H., and Sprunk, G. C., Hydrogenation and Liquefaction of Coal, Part I: Bureau of Mines Tech. Paper 622, 1941, pp. 18-23.

catalyst at 150° C. for 1½ hours, the temperature was increased until the contraction was between 45 and 50 percent or the temperature was 175° C. After 48 hours the temperature was increased to 180° C. as an upper limit for 24 hours. During operation, the contraction was held between 65 and 75 percent.

Iron catalysts 10C, 47C, and 80A were simultaneously reduced and inducted by a special procedure, using $H_2 + CO$ gas mixtures at atmospheric pressure, followed by operation at elevated pressure. The details are given in table 22.

TABLE 22.—*Simultaneous reduction-induction of iron catalysts by special procedures*

Catalyst No	10C	47C	80A.
Test No	62	80	81.
First period:			
Gas mixture	$1H_2+1CO$	$1H_2+1CO$	$1H_2+1CO$.
Time, hours	15	15	15.
Temperature, ° C	240	235	240.
Pressure	Atmospheric	Atmospheric	Atmospheric.
Space velocity, NTP	150	200	200.
Second period:			
Gas mixture	$2H_2+1CO$	$2H_2+1CO$	$2H_2+1CO$.
Time, hours	62.5	25.5	28.5.
Temperature, ° C	240	240	240.
Pressure	Atmospheric	Atmospheric	Atmospheric.
Space velocity, NTP	150	200	200.
Operating conditions:			
Gas mixture	$2H_2+3CO$	$1H_2+1CO$	$1H_2+1CO$.
Temperature, ° C	250	250	250.
Pressure, pounds per square inch	100-135	100	100.
Space velocity, NTP	150	200	200.

Three iron catalysts, 10K, 10M, and 47F, tested in tests X12, X15, and X16, respectively, were reduced by a modification of the slow reduction method as follows: The temperature was slowly raised to 360° C. over a period of 10 hours while hydrogen flowed over the catalyst at a space velocity of 100 per hour. After 4 hours at 360° C. the reduction was concluded. The induction procedure followed a contraction schedule. Synthesis gas was passed over the reduced catalyst at 200° C. and 100 pounds per square inch gage pressure for 1 hour. Contraction was maintained between 45 and 50 percent for 3 days by increasing the temperature at the rate of 3° C. per hour. After the 3-day period an operating contraction, not greater than 60 percent, was maintained by increasing the temperature 20° C. per hour. The maximum operating temperature was 255° C. The tests were operated at a pressure of 100 pounds per square inch.

REACTIVATION PROCEDURES

Standard treatment of the catalysts included reactivation once a week while products were being recovered. This reactivation was used also at any time that the contraction during a test fell below 60 percent for cobalt or 50 percent for iron catalysts, and remained below these limits for 3 hours at maximum permissible temperature (200° C. for cobalt and 260° C. for iron catalysts). Hydrogen was passed over the catalyst at operating temperature for a short time, and then the temperature was raised 10° C. above the operating temperature for 2 hours. The temperature was then lowered to 170° C. for cobalt catalysts and to 220° C. for iron catalysts. Synthesis gas was then admitted and the temperature slowly increased until the desired contraction was obtained.

In a few instances more drastic reactivation procedures were used. One of these consisted in a re-reduction with hydrogen of the catalyst at 400° C. for several hours. Another involved reoxidation by air or oxygen followed by re-reduction with hydrogen. Following these more drastic reactivations it was considered necessary to reinduct the catalyst. Reactivation by solvent extraction was not used in any of these tests.

EFFECT OF VARIATIONS IN METHODS OF CATALYST PREPARATION, REDUCTION, INDUCTION, AND SYNTHESIS CONDITIONS ON ACTIVITY AND DURABILITY

IRON CATALYSTS

Data on iron-catalyst preparation conditions are given in tables 16 to 19, inclusive, and on activity in the synthesis in tables 23 to 27, inclusive. The discussion that follows includes an abstract of the results of recent work by the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr, Germany,[88] on preparation and induction and testing of iron catalysts.

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[88] Leva, M., Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part I. (Technical Oil Mission Reel 101, Document PG-21559-NID, Report on the Middle-Pressure Synthesis with Iron Catalysts): Office of Synthetic Liquid Fuels Report, Pittsburgh, Pa., 1947, pp. 1-48.

TABLE 23.—*Tests on iron catalysts*

[All tests made with pellet catalysts: $1H_2 + 1CO$ at atmospheric pressure.[1] All metal ratios are atomic except in cases of catalysts 15A and 44A, where they are weight ratios]

Catalyst No.	Composition of catalyst	Conditioning procedures		Test No.	Duration of test, hours	Temperature, °C.	Space velocity [2]	Contraction, percent	Hydrocarbon products		Space-time yield [6]
		Reduction	Induction						C_1-C_4 gases,[3] grams per cubic meter [4]	Liquids plus solids,[5] grams per cubic meter	
	UNPROMOTED IRON CATALYSTS										
47A	Fe_2O_3, ex $FeCl_3$, K_2CO_3	Slow	Intermediate	56a	29.3	244	134		Poor activity		
47C	do	do	do	77a	49.5	240	126		do		
47D	do	Special—see table 22		80a	22.6	248			do		
48A	Fe_2O_3, ex $Fe(NO_3)_3$, $NaOH$	Slow	Intermediate	78a	52.5	242			do		
49A	Fe_2O_3, ex sponge iron	do	do	55a	30.7	242	178		do		
50A	Fe_2O_3, ex Lavino iron oxide [7]	do	do	53a	52.3	245	172	7	do		
50B	do [7]	do	Rapid	33a	15.0	272			do		
50C	do [7]	do	Intermediate	45a	17.8	249	148		do		
				b	22.5	241	144		do		
68A	Fe_2O_3, ex limonite ore	do	do	52a	51.5	246	120		do		
68B	do	do	do	47a	19.4				do		
69A	Fe_2O_3, ex $Fe_2(SO_4)_3$, ignited	do	do	63a	76.3	238	162	32	3.4	4.5	0.73
70A	Fe_2O_3, ex $Fe(NO_3)_3$, ignited	do	do	59a	23.0	232			Poor activity		
80A	Fe_2O_3, ex $Fe(NO_3)_3$, KOH	do	do	51a	51.8	245	160		do		
		Special—see table 22		[1] 81a	51.0	249	157	42		63.9	10.05
81A	Fe_2O_3, ex $Fe(NO_3)_3$, Na_2CO_3			b	109.8	249	199	47	1.6	51.2	10.19
				c	118.0	254	202	43	1.0	55.2	11.18
		Slow	Intermediate	64a	43.5	244	147	12	Poor activity		
		do	do	66a	91.8	242	135	14	do		
	PROMOTED IRON CATALYSTS										
1E	$Fe^{+3} : Cu :: 4 : 1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, KOH	Slow	Intermediate	49a	59.0	241	160	30		18.5	2.96
				b	113.6	250	159	21		22.9	3.64
5A	$Fe^{+3} : Cu :: 4 : 1$, ex $FeCl_3$, $Cu(NO_3)_2$, KOH	do	Rapid	29a	128.0	259	140	35	30.3	21.7	3.04
				b	124.6	258	82	36	23.1	27.5	2.26
				c	74.3	253	104	28	9.0	18.9	1.97
6A	$Fe^{+3} : Fe^{+2} : Cu :: 8/3 : 4/3 : 1$, ex$FeCl_3$, $FeSO_4 \cdot 7H_2O$, $Cu(NO_3)_2$, $NaOH$.	do	do	22a	21.4	252			Poor activity		
				b	17.3	260			do		
				c	39.4	270			do		
				d	25.1	266			do		
9A	$Fe^{+3} : Cu :: 4 : 1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, NH_4OH, $(NH_4)_2CO_3$.	do	Intermediate	31a	33.3	254	154	18		12.9	1.99
				b	78.3	262	108	42	52.4	28.3	3.06
				c	122.3	260	108	32	24.4	21.1	2.28
11A	$Fe^{+3} : Cu :: 4:1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, $NaOH$, $Na_2B_4O_7$.	do	Rapid	20a	17.3	247	148	27		12.4	1.83
				b	48.6	261	136	38		27.3	3.72
				c	21.7	284	141	31		13.3	1.88
15A	$FeO : ThO_2 :: 5 : 1$, ex $FeSO_4 \cdot 7H_2O$, $Th(NO_3)_4$, $NaOH$	do	do	30a	37.3	261	161	25	34.3	14.0	2.25
				b	124.3	263	105	23	25.8	13.6	1.43
20A	$Fe^{+3} : Cu : Zn :: 4 : 1 : 1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, K_2CO_3.	do	Intermediate	37a	86.6	251	156	42	34.7	37.8	5.90
				b	92.7	258	144	37	31.5	31.8	4.57
21A	$Fe^{+3} : Cu : Al :: 4 : 1 : 1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Al(NO_3)_3$, K_2CO_3.	do	Rapid	28a	36.4	258	175	27	29.5	11.5	2.02
				b	30.0	265	105	28	47.6	9.8	1.03
22A	$Fe^{+3} : Cu : Cr^{+3} :: 4 : 1 : 1$, ex $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Cr(NO_3)_3$, K_2CO_3.	do	Intermediate	38a	69.4	250	157	17	15.1	5.1	.79
		do	Rapid	34a	12.0	241			Poor activity		
				b	8.1	246			do		
23A	$Fe^{+2} : Cu :: 4 : 1$, ex $FeSO_4 \cdot 7H_2O$, $CuSO_4$, KOH	do	do	27a	45.8	266			do		
24A	$Fe^{+2} : Cu :: 4 : 1$, ex $FeSO_4 \cdot 7H_2O$, $CuSO_4$, K_2CO_3	do	Intermediate	48a	111.8	244	155	45	26.3	53.4	8.28
				[1] 57a	84.9	242	162	52		50.8	8.24
				b	40.5	230	189	57	12.9	59.2	11.17
				c	109.3	230	167	57	10.6	35.4	5.92
				d	91.7	245	165	55	8.6	48.2	7.96
				e	111.4	228	72	75		68.8	4.95
				f	69.3	278	75	80	69.6	92.2	6.91
				g	96.2	249	72	77	75.0	76.6	5.51
				h	95.3	250	65	76	17.9	65.8	4.28
24C	$Fe^{+2} : Cu :: 4 : 1$; $FeSO_4$ (anhydr.), $CuSO_4$, K_2CO_3	do	do	84a	58.1	236	189	15		11.9	2.25
				b	46.0				Poor activity		
25A	$Fe^{+2} : Cu :: 4 : 1$; $FeSO_4$ (anhydr.), $CuSO_4$, $NaOH$, $Na_2B_4O_7$.	do	Rapid	21a	21.5	245	120	14	do		
				b	12.3	251	155	17	do		
				c	48.4	273	154	34		10.4	1.60
39A	$Fe^{+2} : Co :: 4 : 1$; $Fe^{+2}+Co : Cu :: 4 : 1$, $FeSO_4$ (anhydr.), $Co(NO_3)_2$, $Cu(NO_3)_2$, Celite, K_2CO_3, $Na_2B_4O_7$.	do	Intermediate	39a	56.9	238	112	17	22.2	8.6	.86
40A	$Fe^{+3} : Zn :: 4 : 1$; $Fe(NO_3)_3$, $Zn(NO_3)_2$, K_2CO_3	do	do	54a	115.8	250	179	17	11.6	18.6	3.33
43A	$Fe^{+3} : Cu :: 4 : 1$; $Fe_2(SO_4)_3$, $CuSO_4$, K_2CO_3	do	do	61a	25.5	234	122		Poor activity		
44A	$Fe_2O_3 : CrO_3 :: 1 : 4$; $Fe(NO_3)_3$, CrO_3, $NaOH$	do	Rapid	35a	20.5	245			do		
51A	$Fe^{+3} : Th :: 5 : 1$; $Fe(NO_3)_3$, $Th(NO_3)_4$, K_2CO_3	do	Intermediate	50a	42.3	246	119	11	do		
				b	48.3	247	128	12	do		
				c	97.8	252	120	23		16.3	1.96
67A	$Fe^{+3} : Co : Th :: 3 : 2 : 1$; $Fe(NO_3)_3$, $Co(NO_3)_2$, $Th(NO_3)_4$, K_2CO_3.	do	do	58a	45.0	242	161	24	21.1	43.0	6.92
				b	114.6	255	157	25	21.8	18.8	2.95
85A	$Fe^{+2} : Cu :: 4 : 1$; $FeCl_2$, $CuCl_2$, K_2CO_3	do	do	[1] 73a	59.0	242	101	51	18.2	54.7	5.52
				b	100.0				Poor activity		
				c	62.5	245			do		

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[1] Tests 57, 73, and 81a were operated at 100 pounds gage pressure.
[2] Volume of synthesis gas per volume of catalyst per hour.
[3] Stabilized at 0° C.
[4] Grams per cubic meter of feed gas.
[5] Bromine numbers of the liquid products ranged from 35 to 173, the average being 94. Specific gravity of the liquid products ranged from 0.673 to 0.760, with the average at 0.725.
[6] Kilograms of liquid plus solid hydrocarbons per cubic meter bulk volume of catalyst per hour.
[7] The Lavino iron oxide is so-called because it is obtained from the Lavino Co. It is obtained from the sludge remaining after bauxite has been extracted.

TABLE 24.—*Tests on unpromoted iron catalysts*

[Pellets: 1H₂+1CO synthesis gas; slow reduction and intermediate induction for all tests except No. 62 (see table 22 for special conditioning procedure)]

Catalyst No.	Test No.	Duration of test, hours	Temperature, °C.	Pressure	Space velocity [3]	Contraction, percent	Hydrocarbon products											Unreacted gases [2]			
							0° C. stabilizer gases (C_1-C_4)					Liquids plus solids [1]					Space-time yield of liquid plus solid hydrocarbons [5]	Total volume, cubic feet	Volume percent		
							Total volume, liters	Molecular weight	Olefin content, volume percent	Grams per cubic meter [4]	Weight percent of total hydrocarbons	Total weight, grams	Specific gravity, gram per cubic centimeter	Grams per cubic meter [4]	Bromine No.	Weight percent total hydrocarbons			Hydrogen	Carbon monoxide	Nitrogen
10B, Part A.	36a	96.3	248	Atmos.	151	27	4.3	29.8	43.3	7.8	27.0	15.4	0.708	21.1	101	73.0	3.19	18.43	63.4	36.2	0.4
	b	104.9	253	do.	146	38	7.6	33.1	58.0	14.7	25.8	32.3	.737	42.2	110	74.2	6.16	16.67	-----	-----	-----
	c	113.8	258	do.	154	30	16.7	27.6	37.6	23.4	46.7	23.4	.761	26.7	94	53.3	4.11	21.24	59.2	35.5	5.3
	d	66.1	251	do.	159	32	16.3	28.3	30.6	39.2	57.2	15.4	-----	29.4	152	42.8	4.67	12.47	58.0	35.6	6.4
	e	50.8	250	do.	149	33	11.7	25.5	33.0	35.3	55.0	10.9	.742	28.9	107	45.0	4.31	8.79	55.6	40.8	3.6
	f	112.7	233	do.	147	40	25.4	27.0	21.3	37.1	48.2	32.9	.679	39.9	141	51.8	5.86	17.10	57.3	37.2	5.5
Part B.	60a	92.8	242	do.	164	34	3.9	31.2	60.9	7.9	32.1	11.4	.732	16.7	121	67.9	2.74	15.94	45.2	47.5	7.3
Part C.	65a	73.0	240	do.	178	23	3.4	31.4	53.1	8.5	28.8	11.8	.694	21.0	152	71.2	3.74	15.15	40.8	57.6	1.6
	b	43.7	242	do.	136	8						No recovery of products									
10C	79a	89.5	250	do.	126	39	13.6	-----	44.6	40.1	59.3	12.6	.743	27.9	70	40.7	3.52	9.74	54.2	42.7	3.1
	62a	50.8	241	135 p.s.i.a.	155	46	13.0	-----	30.6	-----	-----	25.7	.724	53.3	82	-----	8.26	9.19	44.6	52.4	3.0
	b	66.8	247	135 p.s.i.a.	154	59	14.6	-----	28.3	-----	-----	41.6	.730	66.5	85	-----	10.24	9.02	36.3	52.9	10.8
	c	91.1	250	135 p.s.i.a.	151	48	38.6	26.7	18.1	54.8	43.7	59.1	.716	70.6	78	56.3	10.65	15.18	58.7	38.0	3.3
	d	110.5	254	100 p.s.i.a.	157	62	40.5	34.7	22.2	59.4	47.3	70.0	.714	66.2	80	52.7	10.40	14.13	58.9	40.8	.3
	e	92.3	249	100 p.s.i.a.	98	67	28.5	28.1	10.2	64.2	50.5	34.9	.713	62.9	62	49.5	6.16	6.45	55.6	35.2	9.2
10D	72a	113.5	238	100 p.s.i.a.	184	61	34.0	28.3	19.4	51.6	45.1	52.5	.721	62.8	65	54.9	11.55	11.34	59.8	32.1	8.1
	b	72.0	226	100 p.s.i.a.	106	53	-----	-----	-----	-----	-----	13.8	-----	45.5	-----	-----	4.82	4.97	58.8	36.5	4.7
	c	50.8	249	100 p.s.i.a.	244	88	.6	-----	23.9	-----	-----	9.2	-----	18.6	39	-----	4.54	2.12	60.0	28.8	11.2
	d	111.3	250	100 p.s.i.a.	106	70	1.2	54.4	44.9	6.2	10.9	23.8	.668	50.6	102	89.1	5.36	4.86	89.6	7.6	2.8
10F, Part A.	76a	122.0	252	Atmos.	200	40	33.7	36.9	30.6	56.8	62.2	33.7	.717	34.5	74	37.8	6.90	20.71	49.2	46.7	4.1
Part C.	74a	112.5	245	100 p.s.i.a.	106	59	20.7	30.9	25.2	59.8	53.2	25.1	.716	52.6	69	46.8	5.57	6.91	46.7	48.7	4.6
	b	114.0	244	100 p.s.i.a.	163	47	-----	-----	-----	-----	-----	21.0	-----	28.2	-----	-----	4.60	13.96	-----	-----	-----
	c	22.5	245	100 p.s.i.a.	212	21						No recovery of products									

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[1] Specific gravity and bromine number of liquid product were 0.67–0.76 and 39–152, respectively.
[2] On CO_2- and O_2-free basis.
[3] Volume of feed gas per hour per volume of catalyst.
[4] Grams per cubic meter of feed gas.
[5] Kilograms per cubic meter of bulk volume of catalyst per hour.

TABLE 25.—*Test 25; unpromoted iron*

[Catalyst 10A [1]; pellets; 1H₂ + 1CO [2]; atmospheric pressure; slow reduction; rapid induction]

Test No.	Duration of test, hours	Temperature, °C.	Space velocity [5]	Contraction, percent	Hydrocarbon products									Unreacted gases [4]			
					0° C. Stabilizer gases (C_1-C_4)					Liquids plus solids [3]				Total volume, cubic feet	Volume percent		
					Total volume, liters	Molecular weight	Olefin content, volume percent	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Total weight, grams	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Space-time yield [7]		Hydrogen	Carbon monoxide	Nitrogen
a	7.6	-----	157	16	-----	-----	-----	-----	-----	1.3	22.6	-----	3.55	1.71	-----	-----	-----
b	45.6	263	149	49	-----	-----	-----	-----	-----	15.9	48.4	-----	7.21	5.97	-----	-----	-----
c	21.2	263	129	27	-----	-----	-----	-----	-----	5.4	41.2	-----	5.32	3.36	62.6	30.3	7.1
d	41.6	268	153	25	7.7	27.2	33.1	30.2	53.3	8.1	26.4	46.7	4.04	8.09	-----	-----	-----
e	43.5	261	145	23	-----	-----	-----	-----	-----	6.9	22.7	-----	3.29	8.22	-----	-----	-----
f	-----	-----	-----	-----						No recovery of products							
g	27.0	255	145	18						Do.							
h	78.2	256	115	28	9.5	27.1	42.5	26.2	50.5	11.2	25.7	49.5	2.95	11.06	-----	-----	-----
i	44.8	249	157	23	5.9	26.8	40.5	20.8	33.5	14.0	41.3	66.5	6.48	9.00	63.6	30.7	5.7
j	108.1	256	152	32	12.2	26.7	38.2	20.2	38.6	23.1	32.1	61.4	4.87	16.92	60.0	34.1	5.9
k	53.6	250	154	38	12.5	25.6	32.5	36.0	50.3	14.1	35.6	49.7	5.48	8.52	58.4	37.9	3.7
l	96.0	256	155	30	15.7	24.8	25.7	24.4	43.9	22.2	31.2	56.1	4.84	17.69	-----	-----	-----
m	22.8	230	105	16						No recovery of products							
n	118.8	253	150	32	30.1	32.5	44.8	50.9	58.8	30.5	35.6	41.2	5.34	20.26	64.7	33.1	2.2
o	46.8	259	152	28	10.8	27.5	40.8	40.4	53.4	11.5	35.2	46.6	5.35	8.18	53.0	42.2	4.8

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[1] Ferric hydroxide precipitated by K_2CO_3 from Fe $(NO_3)_3.9H_2O$; 48 cc. catalyst used in this test.
[2] Contains 0.2 percent CO_2, 1 percent CH_4, 2.5 percent N_2.
[3] Specific gravity and bromine number of liquid were 0.70–0.74 and 95–140, respectively.
[4] On CO_2– and O_2–free basis.
[5] Volume of feed gas per hour per volume of catalyst.
[6] Grams per cubic meter of feed gas.
[7] Kilograms per cubic meter of bulk volume of catalyst per hour.

TABLE 26.—*Test 42; unpromoted iron*

[Catalyst 10A+10B [1]; pellets; $1H_2+1CO$ [2] at 100 pounds per square inch gage pressure; slow reduction; intermediate induction]

Test No.	Duration of test, hours	Temperature, ° C.	Space velocity [5]	Contraction, percent	Hydrocarbon products									Unreacted gases [4]			
					0° C. Stabilizer gases (C_1-C_4)					Liquids plus solids [3]				Total volume, cubic feet	Volume percent		
					Total volume, liters	Molecular weight	Olefin content, volume percent	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Total weight, grams	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Space-time yield [7]		Hydrogen	Carbon monoxide	Nitrogen
a	88.5	237	178	36	9.6	29.3	23.1	19.0	45.4	15.1	22.8	54.6	4.06				
b	100.8	247	174	39	12.4	28.7	27.9	21.6	32.6	33.0	44.7	67.4	7.78	15.56	51.4	42.9	5.7
c	101.7	243	167	35	10.9	26.0	18.0	17.8	25.6	36.9	51.8	74.4	8.66	16.13	52.9	44.9	2.2
d	113.1	245	165	44	10.1	22.2	11.7	12.8	17.0	48.9	62.3	83.0	10.28	15.23	56.9	41.4	1.7
e	116.0	247	181	44	17.6	25.0	23.1	22.2	29.5	47.0	53.1	70.5	9.62	17.36	52.0	43.2	4.8
f	117.0	250	182	46	14.0	28.8	30.6	20.2	21.0	67.8	76.0	79.0	13.84	16.64	59.6	38.6	1.8
g	94.5	248	183	49	18.3	32.6	37.7	36.8	35.6	48.2	66.7	64.4	12.20	12.77	58.1	39.6	2.3
h	116.6	248	182	52	21.0	25.3	30.4	26.7	29.5	57.0	63.9	70.5	11.63	14.87	63.5	32.3	4.2
i	116.7	248	177	50	15.7	31.0	32.6	25.0	27.5	57.4	66.0	72.5	11.68	15.28	47.5	46.5	6.0
j	111.8	254	267	51	21.8	30.3	35.0	23.5	31.7	63.7	50.7	68.3	13.35	21.67	46.8	49.2	4.0
k	117.2	244	283	58	16.3	31.5	33.4	16.4	32.8	46.9	33.5	67.2	9.48	20.78	42.9	47.1	10.0
l	91.8	241	183	51	10.9		36.6			41.7	59.1			12.27	51.6	45.6	2.8
m	101.7	244	184	53	18.7	33.4	28.8	35.6	40.5	41.0	52.3	59.5	9.62	12.76	47.5	48.5	4.0
n	93.8	245	175	52						39.9	57.6		10.08	11.62	47.8	49.0	3.2
o	94.2	250	181	69	16.2	32.1	33.7	25.3	30.0	44.2	59.0	70.0	10.69	10.06	50.6	41.8	7.6
p	75.1	246	104	70	15.6	23.0	33.8	51.6	45.3	19.6	62.2	54.7	6.47	3.29	57.4	33.6	9.0

[1] Volume of catalyst used was 42 cc. ferric hydroxide precipitated from $Fe(NO_3)_3 \cdot 9H_2O$ by K_2CO_3 (10A 66⅔ percent+10B, part A, 33⅓ percent by weight).
[2] Contains 3 percent N_2, 1 percent CH_4, 0.3 percent CO_2.
[3] Average specific gravity and bromine number of liquid product were 0.68 and 135, respectively.
[4] On CO_2- and O_2-free basis.
[5] Volume of feed gas per hour per volume of catalyst.
[6] Grams per cubic meter of feed gas.
[7] Kilograms per cubic meter of bulk volume of catalyst per hour.

TABLE 27.—*Tests on unpromoted iron catalysts*

[$1H_2+1CO$ at 100 pounds gage pressure; slow reduction; slow induction with contraction schedule]

Catalyst No.	Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products						CO_2, g./m.^{3} [b]	H_2O, g./m.^{3} [b]
						0° C. stabilizer gases			Liquids plus solids				
						CH_4, g./m.^{3} [b]	C_1-NC_4, g./m.^{3} [b]	Weight percent	G./m.^{3} [b]	Weight percent	Space-time yield [c]		
10K	X-12*a*	141	240	100	32	18.6	34.3	46.6	39.3	53.4	3.93	143.0	15.0
	b	135	241	100	46	6.8	26.5	37.7	43.8	62.3	4.38	165.0	16.0
	c	162	245	100	49	15.7	56.4	51.8	52.6	48.2	5.26	146.6	15.6
	d	163	240	100	49	12.5	([d])	([d])	[d]32.4	([d])	([d])	228.1	24.4
	e	116	248	100	42	12.6	35.4	51.2	33.7	48.8	3.37	182.6	17.7
10M	X-15*a*	164	240	100	8	No product recovery							
47F	X-16*a*	116	250	100	12	Do							
	b	109	246	100	10	-----	-----	-----	3.3	-----	-----	27.2	11.9

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of catalyst per hour.
[d] Sample or part of sample lost.

DELETERIOUS EFFECT OF CHLORIDES ON UNPROMOTED IRON CATALYSTS PREPARED FROM FERRIC SALTS

All the unpromoted iron catalysts in the 47 series prepared from ferric chloride solutions were inactive, regardless of the method of conditioning in the converter (tables 23 and 27). Catalyst 10M, from ferric nitrate but containing chloride, was also inactive (table 27, test X–15). X-ray diffraction data (given in a later section of this paper) showed that these catalysts all contain a large proportion of $\beta Fe_2O_3 \cdot H_2O$ in the freshly prepared, unreduced state, whereas all of the active unpromoted iron catalysts are chiefly αFe_2O_3 and $\alpha Fe_2O_3 \cdot H_2O$. Apparently the catalyst resulting from the reduction and induction of $\beta Fe_2O_3 \cdot H_2O$ is not suitable for catalysis of the hydrocarbon synthesis.

EFFECT OF ALKALI ON ACTIVITY OF UNPROMOTED IRON CATALYSTS

Catalysts 48A and 81A precipitated by sodium hydroxide and carbonate, respectively, were only slightly active. Some work was done at the Kaiser Wilhelm Institute for Coal Research [89] on the effect of alkali additions to unpromoted iron catalysts. The results show that precipitation with sodium carbonate without subsequent addition of potassium carbonate to the washed precipitate yielded catalysts of somewhat lower activity and durability than when potassium carbonate was added to the filter cake. Optimum activity and durability were obtained upon the addition of about 0.25 percent of potassium carbonate to the washed precipitate. In the Bureau of Mines work the active catalysts precipitated with potassium carbonate contained between 0.05 and 0.10 percent of residual potassium (see table 16). The potassium content varied with the rate of precipita-

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[89] Work cited in footnote 88, p. 91.

tion, but the activity of the catalyst in the synthesis appeared to be independent of the potassium content within the limits 0.05 to 0.10 percent.

The Kaiser Wilhelm Institute results also show that iron catalysts precipitated with ammonia without subsequent addition of potassium carbonate are as durable as those precipitated with sodium carbonate to which 0.25 percent potassium carbonate was subsequently added. A larger percentage of paraffin wax in the product was characteristic of the catalysts containing added potassium carbonate as compared with the ammonia-precipitated catalyst.

A possible explanation of the beneficial action of small amounts of potassium carbonate in otherwise unpromoted iron catalysts is that a characteristic spinel structure is preserved when potassium or ammonium ions are present, whereas the sodium spinel is more easily decomposed during the washing of the precipitate. The fact that the Kaiser Wilhelm Institute catalysts prepared by precipitation with sodium carbonate without subsequent addition of potassium were very much more active than Bureau of Mines catalyst 81A is difficult to explain. Possibly the special induction procedure used by the Kaiser Wilhelm Institute activated its catalyst sufficiently to account for this difference. Further experiments are necessary.

EFFECT OF CONDITIONS OF PRECIPITATION OF ACTIVE UNPROMOTED IRON CATALYSTS

The active unpromoted iron catalysts were the 10 and 80A preparations precipitated from ferric nitrate by potassium carbonate and hydroxide, respectively. The conditions of preparation affected the activity of the unpromoted iron catalysts. Rapid precipitation, such as was used in 10F, produced a catalyst with moderate initial activity but a short life of only a few weeks. Rapid drying of the wet catalyst cake in 10B, parts B and C, gave poor catalysts.

The Kaiser Wilhelm Institute reported [90] that iron catalysts precipitated at 20° to 60° C. and not heated to boiling were not as active or as durable as those boiled 1 to 5 minutes. This effect is probably an aging process, resulting in transition from one form of iron hydroxide to another. Most of the Bureau of Mines precipitations of iron hydroxide were made at 70° to 90° C., with a total time of precipitation of 20 to 30 minutes. In the case of catalyst 10F, the time of precipitation was 2 to 3 minutes. The low activity and durability of 10F as compared with the other preparations of catalyst 10 indicate the desirability of some aging of the precipitate.

EFFECT OF DIFFERENT INDUCTION PROCEDURES AND OPERATING PRESSURES FOR UNPROMOTED IRON CATALYSTS

The desirability of the "intermediate" as compared with the "rapid" induction procedure is illustrated by comparison of runs 36 (catalyst 10B, part A) and 25 (catalyst 10A). In test 25 (table 25) at atmospheric pressure, a yield of 48.4 grams of liquid plus solid hydrocarbons per cubic meter of synthesis gas was obtained in the second week of the run at 263° C., which corresponded to a space-time yield of 7.21 kilograms of oil plus wax per cubic meter of bulk

volume of catalyst per hour. From the second to the fifteenth week the production of liquid hydrocarbons tapered off slowly to about 35 grams per cubic meter.

In test 36 (table 24) of catalyst 10B, part A, at atmospheric pressure, the average operating temperature was 250° C., 10° lower than in run 25. The maximum yield (42.2 grams per cubic meter of oil plus wax), obtained in the second week of the test at 253° C., was similar to the high yield in run 25 at 263° C. The maximum space-time yield was 6.16 kilograms per cubic meter of catalyst per hour. The only obvious difference between the two tests was the longer induction period in run 36.

Test 72 (table 24) was a 4-week pressure test (100 pounds per square inch) on catalyst 10D. The highest liquid-plus-solid hydrocarbon yield was 62.8 grams per cubic meter at 238° C., obtained in the first week. This was higher than the first-week yields in other runs on iron catalysts. In the next 2 weeks liquid-hydrocarbon production decreased but increased again to 50.6 grams per cubic meter in the last week of the run at 250° C. The maximum space-time yield was 11.55 kilograms of liquids plus solids per cubic meter of catalyst per hour in the first week. The better yield obtained in run 72 indicated the desirability of pressure operation for longer catalyst life and higher liquid-hydrocarbon productivity.

Other tests on iron catalysts confirmed this observation. Test 42 (table 26) was of 16 weeks' duration, the catalyst used being a mixture of two-thirds catalyst 10A and one-third 10B, part A. This catalyst was inducted and operated at a pressure of 100 pounds per square inch at an average temperature below 250° C. In the second week of the test the liquid hydrocarbon yield was similar to that obtained in a corresponding period in tests 25 (table 25) and 36 (table 24). In succeeding weeks the yield increased, reaching a maximum in the sixth week, at 76.0 grams per cubic meter. This was 1.5 times the maximum yield in tests 25 and 36, which were operated at atmospheric pressure. The maximum space-time yield in test 42 was approximately twice that in tests 25 and 26. The average yield for all of test 42 was about 60 grams per cubic meter.

Because of the absence of certain analytical data on catalyst 10B, a duplicate preparation (10K) was tested in a more recent test (X12, table 27). Induction and operating conditions were similar to those for test 42. During 5 weeks of operation, catalyst 10K showed moderate activity, with yields of 40 to 50 grams per cubic meter at a space velocity of 100 and an average temperature of 240° C. Space-time yields were somewhat lower than those in test 42.

The results of experiments done at the Kaiser Wilhelm Institute [91] on the activity and durability of unpromoted iron catalysts at various pressures show that the optimum pressure for $2H_2+3CO$ gas is 10 to 20 atmospheres. In these experiments, the catalyst was prepared by precipitation from ferric nitrate solution with sodium carbonate. After washing, 1 percent of potassium carbonate (based on dry catalyst) was added to the filter cake, which was then dried. The catalyst was inducted at 1/10 atmosphere and 325° C. with pure CO for 25 hours. Synthesis experiments were conducted at 1, 5, 10, 30, and 60 atmos-

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[90] Work cited in footnote 88, p. 91.

[91] Work cited in footnote 88, p. 91.

pheres pressure of $2H_2 + 3CO$ gas, all of the tests being started at 235° C. The catalyst was virtually inactive at 1 atmosphere pressure during 2 days of testing at 235° to 250° C. At 5 atmospheres contractions of 30 to 40 percent were obtained, but the temperature necessary to maintain this activity was 250° C. on the sixth day and 270° C. on the ninth. At 10 atmospheres a contraction of 50 percent was maintained at 235° to 238° C. for 12 days and at 15 atmospheres for 28 days, whereas at 30 atmospheres for only 3 days, and at 60 atmospheres for only 1 day, before an increase in temperature was necessary. The contractions mentioned in the preceding two sentences were measured without prior removal of carbon dioxide from the end gas. Thus, a 50-percent contraction corresponds to about 80 percent after carbon dioxide removal.

A similar although smaller variation of durability and activity with operating pressure for cobalt catalysts is described in the literature review section of this paper. A possible explanation of the poorer results at 1 atmosphere as compared with 10 atmospheres is that a minimum partial pressure of hydrogen is required to hydrogenate the carbides as they are formed and thus keep active spots free for further carbide formation and hydrogenation. The optimum partial pressure of hydrogen appears to be somewhat higher for iron than for cobalt catalysts. At higher pressures, above about 30 atmospheres, the decreased durability of both iron and cobalt catalysts may be caused by corrosion by metal carbonyl formation and by action of organic acids on the catalyst surface.

In the literature review section of this paper it was noted that increasing operating pressure raises the boiling range of the products from cobalt catalysts. This is also true for iron catalysts. Data showing this effect were obtained by Ruhrchemie[92] and are given in table 28.

TABLE 28.—*Effect of operating pressure on boiling range of product from an iron catalyst*

[Tests made by Ruhrchemie in Germany]

Pressure	atmospheres	1	5	20
CO conversion	percent	95	70	75
Yield of liquid—solid products	grams per cubic meter	90	86	120
Gasoline	percent	57	30	22
Diesel oil	do	24	25	22
Wax	do	19	45	56
Olefins in gasoline	do	68	63	63
Olefins in Diesel oil	do	41	49	46

Tests 62 (table 24) and 81 (table 23), with catalysts 10C and 80A, respectively, both of which were simultaneously reduced and inducted by synthesis gas at atmospheric pressure (see table 22 for induction procedures), were operated at 135 and 100 pounds per square inch, respectively. In the 5-week run of test 62 the first week yielded 53.3

grams per cubic meter at 241° C. The maximum yield was 70.6 grams per cubic meter at 250° C., corresponding to a space-time yield of 10.65 kilograms of oil plus wax per cubic meter of bulk volume of catalyst per hour. When the test was terminated, the production was still high at 62.9 grams per cubic meter. Test 81, of 3 weeks' duration, yielded 51 to 64 grams per cubic meter at 249° to 254° C. and 100 pounds per square inch operating pressure. The space-time yield was 10.05 to 11.48 kilograms of oil plus wax per cubic meter of bulk volume of catalyst per hour.

Tests 62 and 81 may be compared with tests 42 and 72 to look for differences that may be due to the different induction procedures. In tests 62 and 81 a special induction procedure was employed, using synthesis gas at atmospheric pressure and 240° C. for 53 and 77 hours, respectively, whereas in tests 42 and 72 the induction was at 100 pounds gage pressure for 36 hours, during which the contraction schedule outlined on page 89 for the "intermediate" induction procedure was followed. The results show that there is no advantage in the special induction procedure.

The Kaiser Wilhelm Institute,[93] however, reports results which show a decided improvement in activity and durability of iron catalysts using special induction procedures at temperatures in the range 245° to 325° C. and synthesis gas ($2H_2 + 1CO$) at atmospheric pressure or pure CO at 1/10 atmosphere. In the Kaiser Wilhelm Institute work, reaction tubes of 12 millimeters internal diameter were used. The catalyst was distributed evenly over a length of 30 centimeters within the tube, which was placed with its long axis horizontal. The catalyst charge contained 10 grams of iron, corresponding to about 15 cubic centimeters of freshly prepared catalyst. The volume of the reaction zone was 35 cubic centimeters, and hence the catalyst occupied less than one-half of the space. After induction, 4 liters per hour of $2H_2 + 3CO$ gas was passed over the catalyst. In the Bureau of Mines work the reaction zone was an annulus 6.4 millimeters inside and 15.8 millimeters outside diameter and 30 centimeters long, with the long axis of the tube in the vertical position, and contained 40 to 50 grams of catalyst. In the Bureau of Mines tests, after induction, 4 liters per hour of $1H_2 + 1CO$ gas was usually passed through the catalyst bed, but gas throughput was varied in some tests between 4 and 10 liters per hour. The reaction temperatures measured by the Kaiser Wilhelm Institute were those of the aluminum block furnace, whereas those reported by the Bureau of Mines were recorded by a thermocouple embedded in the catalyst.

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[92] Reichl, E. H., The Synthesis of Hydrocarbons and Chemicals from CO and H_2: U. S. Naval Technical Mission in Europe Report 248-45, 1945, p. 46.

[93] Work cited in footnote 88, p. 91.

TABLE 29.—*Kaiser Wilhelm Institute results on induction of iron catalysts precipitated with Na_2CO_3 or NH_4OH, washed, and mixed with 0.25 percent (of their dry weight) of K_2CO_3*

[(A) Induction and synthesis with $2H_2 + 3CO$ at 15 atmospheres. (B) Induction $2H_2 + 1CO$, 1 atmosphere, 245° C., for 5 days; synthesis with $2H_2 + 3CO$ at 15 atmospheres. (C) Induction with $2H_2 + 3CO$ at 1/10 atmosphere, 325° C., 25 hours; synthesis with $2H_2 + 3CO$ at 15 atmospheres. (D) Induction with pure CO at 1/10 atmosphere, 325° C., 25 hours; synthesis with $2H_2 + 3CO$ at 15 atmospheres]

(Contraction values include CO_2 content)

Days		1	2	4	5	7	10	11	13	14	20	28	30	40	50	60	69	70	75
Temperature ° C.	A	245	-----	245	250	253	-----	260	270	275	-----	280	-----	-----	-----	290	268	-----	280
Contraction percent		4	-----	10	13	17	-----	24	24	37	-----	36	-----	-----	-----	50	37	-----	47
Liquids − solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	B	245	245	250	250	-----	252	-----	-----	-----	256	-----	-----	-----	255	-----	-----	-----	-----
Contraction percent		59	48	53	49	-----	46	-----	-----	-----	51	-----	-----	-----	51	-----	-----	-----	-----
Liquids − solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	109	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	C	235	-----	-----	235	-----	235	-----	-----	-----	235	-----	237	240	240	241	-----	247	-----
Contraction percent		56	-----	-----	56	-----	56	-----	-----	-----	52	-----	48	52	50	48	-----	53	-----
Liquids − solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	D	235	235	-----	235	-----	235	-----	-----	-----	235	-----	-----	-----	235	-----	-----	-----	-----
Contraction percent		47	50	-----	50	-----	51	-----	-----	-----	55	-----	-----	-----	54	-----	-----	-----	-----
Liquids − solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	105	-----

Days		80	90	98	100	106	110	120	130	140	150	160	170	180	190	200	250	300	350
Temperature ° C.	A	-----	280	283	-----	285	-----	-----	288	292	298	-----	-----	-----	-----	-----	-----	-----	-----
Contraction percent		-----	49	44	-----	43	-----	-----	43	44	47	-----	-----	-----	-----	-----	-----	-----	-----
Liquids − solids g/m³		-----	-----	-----	-----	96	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	B	-----	-----	-----	265	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Contraction percent		-----	-----	-----	55	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Liquids + solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	C	250	249	-----	252	-----	248	256	264	269	270	270	277	278	272	273	-----	-----	-----
Contraction percent		54	53	-----	52	-----	48	48	56	47	53	47	44	43	46	47	-----	-----	-----
Liquids − solids g/m³		-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Temperature ° C.	D	-----	-----	-----	235	-----	-----	-----	235	245	-----	250	-----	251	-----	250	265	263	270
Contraction percent		-----	-----	-----	53	-----	-----	-----	47	48	-----	49	-----	50	-----	44	50	43	40
Liquids + solids g/m³		-----	-----	-----	110	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	110	-----

Table 29 contains data obtained by the Kaiser Wilhelm Institute for activity of an iron catalyst using four different induction procedures. These data are not directly comparable with the Bureau of Mines results presented in tables 24 and 26, chiefly because the contractions reported in table 29 are measured without prior removal of carbon dioxide. The Kaiser Wilhelm Institute data of table 29 show that induction with pure CO at 1/10 atmosphere and 325° C. for 25 hours is the best of the four procedures used. The Kaiser Wilhelm Institute report [94] contains data which show that 325° C. and 1/10 atmosphere are the optimum induction conditions when pure CO is used. These data show also that the space velocity of the CO, which was 4 liters per hour in case (D), may be increased to 40 liters per hour and the total time of induction decreased from 25 to 2.5 hours.

During the 65 days of operation in test 42 (table 26) none of the difficulties which the Kaiser Wilhelm Institute report [94] describes as accompanying the use of a vertical bed of catalyst were noted. Although some "swelling" of the pellets was observed upon discharging the catalyst in test 42, there was no indication that the operation could not have been continued for a much longer period. It is possible that the special induction procedure used by the Kaiser Wilhelm Institute resulted in a catalyst which accelerated the rate of the carbon-forming reactions.

TESTS ON PROMOTED IRON CATALYSTS

An active and durable promoted iron catalyst was 24A, tested in test 57 (table 23). This catalyst was prepared by precipitation with potassium carbonate from ferrous and cupric sulfate solutions. During 25 days of operation contractions of more than 50 percent were obtained at temperatures of 230° to 250° C. The space-time yields were, however, no greater than those with the unpromoted catalyst. Catalyst 85, prepared from ferrous and cupric chlorides, and 67A, from ferric, thorium, and cobalt nitrates, showed fair initial activities which dropped sharply during the second week of operation (see table 23).

Experiments on promoted iron catalysts at the Kaiser Wilhelm Institute [95] confirm the conclusion that additions of thoria, alumina, manganese oxide, or zinc oxide to the iron catalyst do not enhance its activity or durability. These experiments include some work on carriers such as kieselguhr, alumina, and chromium oxide. Chromium oxide appears to be an inert carrier, whereas alumina and kieselguhr, when present in appreciable quantities, are detrimental to the activity of iron catalysts. Kieselguhr, however, has one desirable effect when used in an iron catalyst, namely, an appreciably higher water : carbon dioxide ratio in the products is obtained. Filtration and washing of ferric hydroxide are aided by the presence of kieselguhr. It was found that the addition of small amounts of potassium carbonate to iron-kieselguhr catalysts did not activate them as in the case of iron catalysts with no kieselguhr.

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[94] Work cited in footnote 88, p. 91.

[95] Leva, M., Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis, Part I. (Technical Oil Mission Reel 101, Document PG-21581-NID, Recent Investigations on Iron Catalysts); Office of Synthetic Liquid Fuels Report, Pittsburgh, 1947, pp. 68-158.

It is perhaps significant that a few of the reportedly "best" iron catalysts developed in Germany in recent years contain a small proportion of kieselguhr. These catalysts also contain an appreciable amount of calcium oxide or alumina and small amounts of potassium oxide.[96] The details of preparation of a Ruhrchemie Fe–Cu–CaO–kieselguhr catalyst are given in the Appendix. This catalyst was reduced at 300° C. with $3H_2+1N_2$ gas at a space velocity of 3,000 volumes of gas per volume of catalyst per hour, for about 1 hour. The reduction occurs in stages, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. It is stated that the reduced catalyst contained some of each of these compounds but not more than 5 to 8 percent of metal (Fe) based on the total iron present. The content of Fe+FeO, as determined by solubility in boiling 2-percent acetic acid, should not exceed 65 to 75 percent. The catalyst was inducted at 1 atmosphere and 130° C. for 12 to 24 hours. This catalyst when operated at 15 atmospheres of 1.26 H_2+1CO and 230° C. yielded a large proportion of wax. The contraction was 60 percent; CO conversion 80 percent; $CO:H_2$ consumption ratio 1 : 1.24; CO converted to CO_2, 25.6 percent; CO converted to CH_4, 7 percent. The yield in grams per cubic meter of feed gas was 135 grams of liquids plus solids and 10 grams of C_3+C_4. It was calculated that addition of a second stage of operation would increase these figures to 168 and 13 grams, respectively. The product distribution was as follows:

	End point, ° C.	Percent by weight	
Gasoline	200.	16	70 percent olefins.
Diesel oil	200–320.	20	
Soft wax	320–460.	22	
Hard wax	Above 460.	42	

These data were obtained from a report cited above.[97]

A sample of Ruhrchemie Fe–Cu–CaO–kieselguhr, 100 : 2.5 : 10 : 15 parts by weight, catalyst was captured by the Technical Oil Mission,[98] and tested by the Bureau of Mines (test X39, table 30). In text X39 the catalyst was not reduced. The induction procedure was different from that described by Ruhrchemie [99] and consisted of treatment with $2H_2 + 1CO$ gas at 255° C. for 3 days. The sample container was crushed during shipment, and all of the catalyst had spilled into the outer wooden packing box. Only about 10 percent of the original sample was recovered, the bulk of it having been lost in transit. It is possible that some contamination may have occurred during shipment. In test X39 the maximum yield was 90.6 grams per cubic meter of liquid hydrocarbons (pentane and higher) as compared with 135 grams reported by Ruhrchemie. The $C_3 + C_4$ yield in test X39 was about 16 grams per cubic meter as compared with 10 grams per cubic meter in Ruhrchemie's test.

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[96] Technical Oil Mission Reel 42, Experiments (1944) 657 to 808: Bag 3439, Item 22.
Technical Oil Mission Reel 33, Official Test of Six Iron Catalysts: Bag 3440, Item 29.
Technical Oil Mission Reel 37, Minutes and Other Products Covering Development of Fe Medium Pressure Synthesis 1937–1944: Bag 3451, Item 24.

[97] Work cited in footnote 92, p. 100.

[98] Sample 234, memorandum by W. F. Faragher on samples secured on Combined Intelligence Objectives Subcommittee Trips 551 and 551A, June 25 to July 15, 1945, and subsequent Field Information Agency, Technical trips, July 25 to Sept. 9, 1945. Samples from Ruhrchemie Oberhausen/Holton secured Sept. 3, 1945.

[99] Work cited in footnote 92, p. 100.

TABLE 30.—*Test X–39: 51.0 grams of T. O. M. catalyst (Fe : Cu : CaO : kieselguhr :: 100 : 2.5 : 10 : 15 parts by weight)*

[Sample 234, granules; inducted 3 days at 255° C., with 1 atmosphere of $2H_2 + 1CO$; operated at 100 p. s. i. of $1H_2 + 1CO$, except in test *a*, where the pressure was atmospheric]

Test No.	Duration of test, hours	Average temperature, °C.	Space velocity [1]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g/m.³ (2)	Hydrocarbon products: 0° C. stabilizer gases: C_2, g/m.³ (2)	Hydrocarbon products: 0° C. stabilizer gases: C_3+C_4 g/m.³ (2)	Hydrocarbon products: 0° C. stabilizer gases: Weight, percent	Hydrocarbon products: Liquids plus solids: g/m³ (2)	Hydrocarbon products: Liquids plus solids: Weight, percent	Hydrocarbon products: Liquids plus solids: Space-time yield [3]	CO_2, g/m.³ (2)	H_2O, g/m.³ (2)
a	74	254	96	53	9.3	10.3	8.4	37.6	46.4	62.4	4.45	278.9	42.4
b	114	234	99	65	34.9	2.4	15.7	36.9	90.6	63.1	8.97	374.9	14.2
c	115	233	99	61	8.3	5.6	14.6	28.2	70.0	71.8	6.93	275.3	21.2
d	115	236	100	60	8.7	4.3	17.4	28.5	76.4	71.5	7.64	291.4	15.7
e	115	233	99	56	10.6	8.0	17.5	34.0	70.2	66.0	6.95	251.1	14.0
f	115	233	100	60	9.6	5.0	18.6	30.8	74.4	69.2	7.44	298.7	19.1

[1] Volume of feed gas per hour per volume of catalyst.
[2] Grams per cubic meter of feed gas.
[3] Kilograms per cubic meter of catalyst per hour.

Tables 31 and 32 contain data on comparative tests [1] [2] of six iron catalysts, the tests being conducted at the Braunkohle-Benzin A. G. in Schwartzheide-Ruhland. One catalyst was submitted by each of the following organizations: Kaiser Wilhelm Institute, Lurgi, Brabag, I. G. Farbenindustrie, Ruhrchemie, and Rheinpreussen. The tests were conducted using a single unit of the standard middle-pressure reactor. This unit consists of two concentric tubes with the catalyst packed into the annulus between them and with cooling liquid circulated outside the outer tube and inside the inner tube. The

TABLE 31.—*Composition of iron catalysts used in comparative tests at Braunkohle-Benzin A. G., Schwartzheide-Ruhland*

[All figures are based on 10-cubic meter catalyst volume]

Company	Apparent density, kilograms per liter	Fe, tons	Cu	Zn	K_2CO_3, percent of iron	Carrier	Reduction and induction
			Kilograms				
Kaiser Wilhelm Institute.	1.02	6	60		0.75	None	$2H_2+1CO$, 325° C.
Lurgi	.79	3.9	390		30 percent K_4SiO_4.	SiO_2 (water glass).	H_2, 30 percent reduction.
Brabag	1.37	6.9	690	690	0.5	None	Water gas at 245° C. H_2 or synthesis gas at 225° C.
I. G. Farbenindustrie.[1]	2.27	18.0			1.0	do	H_2 at 500° C.
Ruhrchemie	.44	2.5	125		0.5–2.0	K'ghr	H_2.
Rheinpreussen	.68	2.7	135		0.5–1.0	Ground dolomite.	H_2 300°–400° C. Water gas, 245° C.

[1] Contained 2 percent Al_2O_3+CaO.

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[1] Work cited in footnote 92, p. 100.

[2] Technical Oil Mission Reel 134, Minutes of meeting, Sept 5, 1944 (Reichsamtsversuche): Sec. 1b, item 24.

annulus was 24 millimeters in inside diameter and 44 millimeters outside diameter, and 5 meters over-all length. The tube was water-jacketed, with a vapor chamber connected to the top by means of which steam pressure could be controlled to obtain the desired synthesis temperature. The highest permissible temperature in these tests was 225° C.; the operating pressure was 10 atmospheres of $1.25H_2+1CO$ gas (containing 12 percent inert gas). The analysis of the synthesis gas showed 6.2 percent CO_2, 39.2 percent CO, 48.8 percent H_2, 2.6 percent CH_4, and 3.2 percent N_2. The duration of the tests was 3 months. The temperature and space velocity were independently varied by each operator to secure optimum yields and durability. At the end of 2 weeks, all units had reached about 200° C. The space velocities were in the range 105 to 110 volumes of synthesis gas per volume of catalyst per hour.

TABLE 32.—*Cooperative tests on iron catalysts at Schwartzheide*

[10 atmospheres; 200°–225°C.; synthesis gas contained 12 percent inerts and 88 percent $1CO+1.25H_2$; yields per cubic meter are based on feed gas. Space velocity is volumes (N. T. P.) of feet gas per volume of catalyst per hour. Other data are in weight percent unless otherwise specified]

	Kaiser Wilhelm Institute	Lurgi	Brabag	I. G. Farbenindustrie	Ruhrchemie	Rheinpreussen
Space velocity	109	107	111	115	104	104
CO conversion	85	88	77	81	70	62
CO : H_2 consumption ratio	.80	.66	.69	.74	.72	1.07
Maximum yield . grams per cubic meter	147	142	141	144	147	168
Average yield ... do.	125	124	108	117	103	104
Average yield ... tons per day	3.26	3.19	2.88	3.23	2.57	2.00
Wax:						
Saturates	17.6	24.7	34.4	16.9	21.7	11.6
Olefins	.2	4.5	4.8	2.6	2.0	.3
Oxygenated	.3	6.0	3.8	1.5	1.9	1.2
Diesel oil, C_{11} to C_{18}:						
Saturates	11.5	3.9	5.1	4.2	6.3	10.5
Olefins	2.1	5.2	7.7	5.1	3.0	2.6
Oxygenated	.6	4.1	3.5	1.9	3.5	.4
Gasoline, C_5 to C_{10}:						
Saturates	11.7	6.3	4.6	8.1	8.9	14.2
Olefins	12.1	10.0	11.8	15.1	9.8	14.2
Oxygenated	1.2	3.1	1.2	2.2	3.5	1.2
C_3+C_4:						
Saturates	9.5	4.1	2.5	5.4	5.5	10.0
Olefins	10.4	8.1	8.1	13.2	9.0	11.5
CH_4	8.0	5.6	3.8	9.0	7.0	8.1
C_2H_4	.9	2.7	2.2	2.8	2.2	.7
C_2H_6	7.8	2.6	2.3	4.9	4.4	8.1
C_1 to C_3 alcohols	6.1	9.1	4.2	7.1	11.3	5.4
Kg. C_5+ per hour per cubic meter of catalyst	10.9	11.6	10.8	10.9	8.8	8.5

Only three of the six catalysts operated 90 days with one filling of catalyst. The others encountered "coking" difficulties and had to renew the charges repeatedly (four times in the case of Rheinpreussen). A description of the method of preparation of only one of the catalysts was found. The catalyst submitted by the Kaiser Wilhelm Institute was prepared in the following way: The iron was precipitated from a dilute nitrate solution (1 kilogram of iron in 30 liters) at 70°C. by additions of boiling soda solution (1 kilogram of soda in 10 liters). One percent of copper (based on the iron) has been added to the iron solution before precipitation. The iron nitrate solution contained approximately equimolar proportions of ferric and ferrous nitrates. The precipitate was filtered and washed with hot distilled water until free from alkali. A paste was then made with distilled water, and a solution of potassium carbonate (containing 0.75 percent of potassium carbonate, based on the iron) was mixed with the paste. Thickening of the paste was effected on a water bath and drying completed at 105°C. in an oven. The dried pieces were then broken into granules of 2–4 millimeters.

The catalyst was pretreated as follows: A mixed gas, rich in hydrogen ($2H_2+1CO$), was passed over the catalyst for 24 hours at a pressure of 1/10 atmosphere and a temperature of 325°C. (8 liters of gas per hour per 10 grams of iron). The strongly pyrophoric catalyst was then soaked in paraffin wax to protect it from oxidation and put into the converter with as little contact with air as possible.

At the beginning of the synthesis, the catalyst was very active at 185° to 190°C. To maintain a high conversion throughout the 3-month test, the temperature was raised gradually from 195° to 224°C., most of the operation being conducted between 215° and 220°C.

The Ruhrchemie catalyst was probably prepared in the manner described in the Appendix for the Fe:Cu:CaO:kieselguhr. The Lurgi catalyst was probably similar or identical with those described in reference 414. , The composition of the best Lurgi iron catalysts is reported as 100 Fe, 5 to 10 Cu, 9 Al_2O_3, 9 K_2O, 24 SiO_2. The boiling solution of iron, copper, and aluminum nitrates is precipitated by adding soda solution until a *p*H value of 9 is attained. The precipitate is washed by decantation and then centrifuged. Potassium silicate solution is then added and the catalyst dried and crushed to size. Reduction is conducted at 250° to 300° C. with hydrogen at a space velocity (per hour) of about 35 for about 40 minutes. The reduced catalyst contains 25 to 30 percent of metallic iron.

The I. G. Farbenindustrie catalyst was fused Fe_3O_4 containing 2 percent Al_2O_3+CaO and 1 percent K_2CO_3. Complete reduction of the I. G. catalyst is essential. This is effected by hydrogen at 450° to 500° C. and a high space velocity for 48 to 72 hours. The Brabag, Ruhrchemie, and Rheinpreussen catalysts were probably precipitated from nitrate solutions. The presence of about 35 percent of calcium carbonate in the Rheinpreussen catalyst may have been responsible for the relatively rapid formation of carbon. The silica and kieselguhr in Lurgi and Ruhrchemie catalysts also are known to decrease the durability of iron catalysts.

The CO:H_2 consumption ratios given in table 32 show that 50 percent or more of the oxygen appeared as water. This is much greater than the yield of water reported in test X39 (table 30) and by the Kaiser Wilhelm Institute.[3][4] The yields of liquid products obtained from the Kaiser Wilhelm Institute and the Lurgi catalysts were only about 20 percent below those recorded for cobalt catalysts at 10 atmospheres. The highest yields of wax were obtained from the Lurgi

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[3] Work cited in footnote 88, p. 91.
[4] Work cited in footnote 95, p. 103.