Discussion of Results

The highest yields in experiment 17 were obtained during the first 48 to 72 hours, when the temperature of the steam entering the heating jacket of the convertor was 201° to 202° C.; a maximum yield of 302 l. of water and 192 l. of primary liquid product (oil) was obtained. During the first 24 hours of operation, an apparent contraction of 58.2 percent was observed with the production per cubic meter of synthesis gas of 160 ml. of water, 103 ml. of oil, and 10 l. of gasol; correction for the inerts content of the synthesis gas gives an actual contraction of 66.5 percent and corresponding product values of 180 ml. of water, 120 ml. of oil, and 12 l. of gasol per cubic meter of pure $2H_2:100$ gas. The activity of the pilot-plant catalyst, therefore, was comparable to the activities found in small, bench-scale tests. To compensate for a gradual loss in catalyst activity, the operating temperature was gradually increased from 200° to 215° C.; after continuous operation for 336 hours, experiment 17 was terminated. Photographs of the reactor and auxiliary equipment are shown in figure 30, 31, and 32.

The results of experiment 17 are listed in table 9. For an average apparent contraction of 56.2 percent, a total production of 4,485 l. of water, 258 l. of paraffin hydrocarbons, 538 l. of Diesel oil, and 1,472 l. of gasoline (2,268 l. total oil) were obtained from 26,729 m.3 of synthesis gas. Calculations showed that the actual synthesis gas velocity during the experiment averaged only 79.6 m.3/hr. instead of the 100 m.3/hr. indicated by the gas-meter. The difference may be attributed to meter calibration, temperature, and pressure corrections, and to a slight gas leak at the exit of the blower. Incorporating this correction into previous calculations produced the following average results per cubic meter of synthesis gas:

TABLE 9. - Results of Experiment 17

Experiment life, days	Hot H_2O, °C.	Reaction temperature, °C.	Volume of synthesis gas used, m.3	Gas velocity, m.3/hr.	Contraction, percent	Liquid products, liters/day					Gasol m.3/day	Gaseous products, ml./m.3		
						H_2O	Paraffin	Diesel oil	Gasoline	Total oil		H_2O	Oil	Gasol
1........	201.5	202.5	1,837	76.5	52.4	285	19	32	83	134	19	155	73	10
2........	202	204.5	1,872	78.0	58.2	315	22	44	97	163	21	168	87	11
3........	202	206.5	1,865	77.7	58.2	302	35	47	110	192	18	160	103	10
4........	202	207	1,859	77.4	57.7	307	23	45	105	173	18	165	93	10
5........	203	207	1,832	76.4	58.6	299	22	43	105	170	17	163	93	9
6........	203	208.5	1,848	77.0	55.1	295	22	42	103	167	15	160	90	8
7........	206	210	1,843	76.8	60.8	321	19	43	110	172	12	174	91	7
8........	207	211	1,815	75.6	61.9	311	17	43	110	170	16	171	94	9
9........	208	212	1,974	82.3	58.6	343	16	41	113	170	10	174	86	5
10........	209	212.5	2,009	83.3	55.3	355	14	40	110	164	14	177	82	7
11........	209	213	1,990	82.9	54.7	343	13	36	108	157	10	172	79	5
12........	210	213.5	1,979	82.4	53.2	342	13	37	112	162	11	173	82	5
13........	211	213	2,005	83.5	53.2	339	12	33	110	155	9	169	77	4
14........	211	214	2,001	83.4	50.3	331	11	32	96	139	10	165	70	5
Total.....	-	-	26,729	-	-	4,488	258	558	1,472	2,288	-	-	-	-
Average...	-	-	-	79.6	56.2 a/(66.5)	-	-	-	-	-	14.5	168 a/(199)	86 a/(102)	7 a/(8)

a/ These values computed on basis of inert-free synthesis gas.

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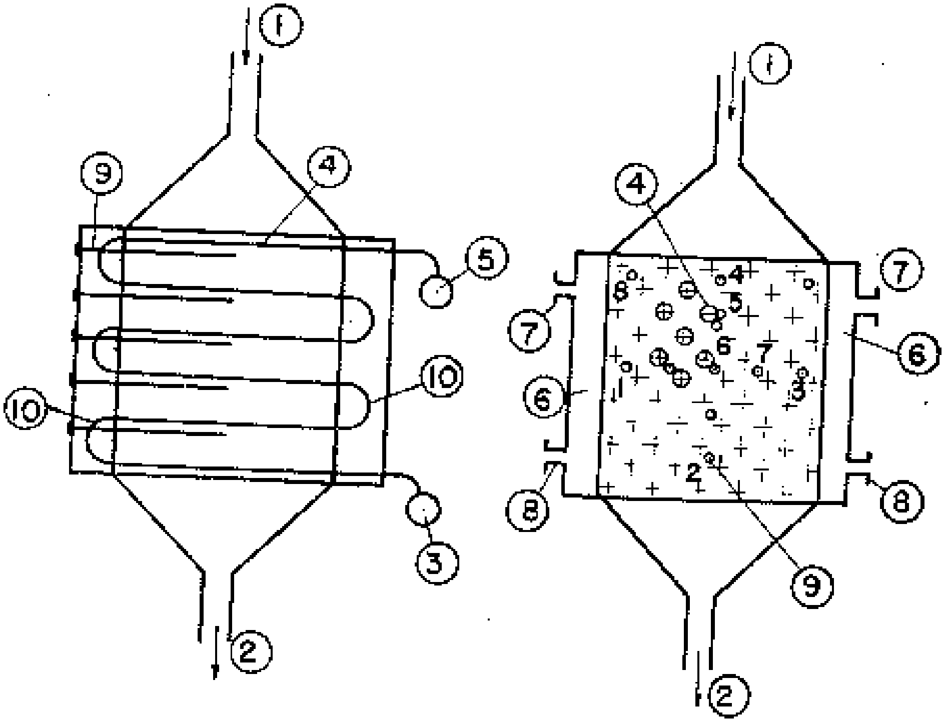

1 Synthesis gas inlet
2 Outlet for product gas and unreacted synthesis gas
3 Cooling water distributor
4 Cooling tubes
5 Hot water collector
6 Heating jacket
7 Outlet from heating jacket
8 Inlet to heating jacket
9 Thermocouple tubes
10 Cooling tube return bends

Points 1,2,3,4,5,6,7 and 8 designate points of temperature measurement.

Figure 33. - Thermocouple locations in 100 m.^{3}/hr. converter.

Synthesis gas containing 15.5 percent inert gases: 168 ml. water, 86 ml. oil, 7 l. gasol.

Inert-free synthesis gas: 199 ml. water, 102 ml. oil, 8 l. gasol.

The heating schedule for the catalyst bed is shown in table 10, and simultaneous temperatures at different points in the heating jacket are listed in table 11 (the location of these points is shown in figure 33).

Table 10.- Temperature schedule in catalyst bed[a]

Experiment life, hours	Steam temperature, °C.		Catalyst bed temperature, °C.								Synthesis gas velocity, $m.^3$/hr.	Apparent contraction, percent
	In	Out	1	2	3	4	5	6	7	8		
0	199	198	200	200.5	199.5	200.5	202.5	200	200.5	201.5	86.5	22.5
4	200	201.5	200	200	200	202.5	204.5	200	202	204.5	87.6	54.9
16	201.5	202	204	201.5	201.5	206.5	206.5	201.5	205	205	86.9	54.0
28	202.5	203	201.5	192.5	199.5	204	206.5	204.5	202	206.5	84.5	57.3
40	201.5	201.5	203.5	194.5	201	203.5	206.5	203.5	203.5	204.5	89.4	56.2
52	202	203	204	193	201.5	204	206.5	204	204.5	204.5	88.0	60.2
64	202	203	208	206.5	206.5	206	207	204	206.5	206	86.6	56.4
76	202	203	207.5	207.5	208.5	204.5	207	204	206.5	205	84.9	58.0
88	202	202	209	209	206.5	206.5	206.5	204	204	204	86.4	56.4
100	202	203	207	206.5	206	204	205.5	204	206.5	206	90.4	58.5
112	203	204	206	206.5	206.5	206.5	206	204	205	204	83.1	58.3
124	203	204.5	208	208	206.5	206.5	207	205	206	204	89.9	60.5
136	203	203.5	206.5	206.5	206.5	205	207	204	206.5	205	87.6	52.1
148	206	206	210.5	211.5	209.5	209	211.5	206.5	211.5	209.5	88.8	62.3
160	206	206	211.5	211.5	209.5	209.5	211.5	208	211.5	210	88.1	57.6
172	207	208	212	211.5	211	211.5	212	209	213	209	81.2	59.3
184	207	207.5	210.5	210.5	208.5	207	211.5	208.5	210.5	207	88.6	56.3
196	208.5	209	213	212	211.5	209.5	213	209	211.5	210	96.0	55.2
208	208	209	211.5	211.5	211	209.5	213	209	212.5	209.5	96.6	52.0
220	209	210	214.5	215.5	213	211.5	214.5	210	213	211.5	94.0	58.0
232	209	209.5	212	211.5	210	209.5	214	211.5	211.5	209.5	92.6	52.5
244	208.5	209	214.5	212	211.5	211.5	215.5	212	211.5	209.5	91.5	58.6
256	209	209.5	214	211.5	209.5	210	214	210.5	210	209	93.2	52.5
268	210	211	215	214.5	212	214.5	215.5	211.	211.5	211.5	93.8	55.3
280	210	210.5	215.5	214.5	211.5	211.5	214.5	212	211.5	210	91.7	49.0
292	211	212	214.5	213	211.5	211.5	214	213	213	211.5	92.8	53.7
304	211	211.5	214.5	214	211.5	211.5	214.5	213	211.5	211	92.5	54.1
316	211	211	214.5	213.5	211.5	211.5	214	213	211.5	211.5	94.0	53.5
328	211	211.5	214	211.5	211.5	210	214.5	213.5	211.5	210	93.3	48.0

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a/ No corrections made for temperature.

TABLE 11. - Temperature distribution in converter

Distance from center, cm.[a]	Points of temperature measurement[b]					
	1	2	4	5	7	8
0	216	214	209.5	214.5	214.5	211.5
10	217	211.5	211.5	214.5	214.5	211.5
20	216.5	212	212.5	214.5	214.5	211.5
30	215.5	213	213	214.5	214.5	211.5
40	215.5	214	213	214.5	214.5	212
50	215.5	211.5	213	214.5	213.5	214.5

[a] Temperatures measured at points moving progressively from center toward cooling coil bends (see fig. 1).

[b] Distribution of thermocouple locations shown in figure 1.

The analyses of samples of the gaseous mixture leaving the converter are listed in tables 12 and 13 and indicate that the extent of side reactions has been small. Comparison of these results with those of small, bench-scale experiments (table 14) indicates that more satisfactory yields are obtained in a large-scale operation. These results suggest that commercial synthesis of gasoline and hydrocarbon oils from carbon monoxide and hydrogen will be successful.

Table 12.- Synthesis- and product gas analyses.

Experiment life, hours	Synthesis gas, volume-percent							Product gas, volume-percent						
	CO_2	O_2	CO	H_2	C_nH_{2n+2}	N_2	"Useful gas"	CO_2	O_2	C_mH_n a/	CO	H_2	C_nH_{2n+2}	N_2
0	7.2	0.3	28.4	54.9	2.3	6.9	82.4	14.0	0.1	0.0	21.5	45.0	9.3	10.1
5	7.7	.1	27.4	56.3	2.2	6.3	82.2	19.4	.0	.2	19.4	39.2	12.1	9.7
17	5.2	.1	30.4	56.0	1.8	6.5	84.0	13.1	.0	.2	24.8	41.0	9.3	11.6
29	6.1	.1	28.7	56.5	1.6	7.0	84.8	16.9	.0	.4	21.3	35.4	12.9	13.1
41	6.2	.2	29.0	56.8	1.9	5.9	85.2	14.9	.1	.4	24.0	36.8	12.7	11.1
53	6.0	.2	28.2	57.5	1.5	6.6	84.6	17.0	.1	.3	22.3	27.7	11.8	10.8
65	6.3	.2	28.2	57.9	1.0	6.4	84.6	16.5	.2	.7	21.4	37.6	14.1	9.5
77	7.3	.1	26.9	57.2	1.5	7.0	80.7	19.9	.3	.3	19.4	37.9	12.1	10.1
89	7.0	.2	27.8	55.3	2.0	7.9	82.8	16.6	.2	.6	19.8	37.6	13.8	11.4
101	7.4	.1	28.9	56.5	1.3	5.8	84.7	18.2	.2	.3	22.2	37.2	11.5	10.4
113	6.7	.1	27.0	57.5	1.7	7.0	81.0	17.0	.2	.9	17.2	36.6	16.5	11.6
125	7.4	.2	26.4	56.2	1.5	8.3	79.2	18.6	.1	.4	21.0	36.1	11.7	12.1
137	7.2	.1	28.4	55.6	1.6	7.1	83.5	15.2	.1	.7	23.5	37.9	12.1	10.5
149	7.4	.2	27.7	53.5	2.9	8.3	80.3	22.8	.3	.4	15.2	29.1	18.5	13.7
161	7.0	.1	28.6	57.5	1.3	5.5	85.8	18.1	.1	.5	19.9	30.7	19.4	11.3
173	6.8	.2	28.8	54.8	2.6	6.8	82.2	21.2	.0	.4	18.0	29.0	19.0	12.4
185	7.1	.1	28.0	57.1	1.5	6.2	84.0	18.7	.0	.8	18.8	30.4	20.5	11.2
197	7.6	.2	27.5	56.9	1.6	6.2	82.5	20.6	.1	.5	16.8	34.0	17.4	10.6
209	7.0	.1	28.3	56.8	1.3	6.5	84.9	16.5	.0	.6	20.6	36.6	17.1	8.6
221	7.9	.2	27.7	55.8	2.6	5.8	83.1	20.8	.1	.2	16.7	32.0	18.6	11.6
233	7.5	.1	27.9	56.0	1.9	6.6	83.7	18.0	.1	.8	18.6	32.1	20.6	9.8
245	7.4	.2	27.2	57.0	2.3	5.9	81.3	20.7	.1	.7	14.8	31.5	20.4	11.8
257	7.0	.0	27.8	57.2	2.4	5.6	83.4	17.8	.0	1.0	19.2	32.7	18.6	10.7
269	7.4	.2	28.0	57.0	1.3	6.1	84.0	20.3	.0	.5	16.4	30.9	20.2	11.7
281	7.4	.1	28.1	56.4	1.6	6.4	84.3	16.8	.2	.7	21.5	34.3	17.5	9.0
293	6.8	.2	28.8	55.3	1.9	7.0	83.0	19.0	.2	.4	18.8	31.0	19.1	11.5
305	6.8	.1	28.3	57.3	1.2	6.3	84.9	15.9	.1	1.0	19.6	35.7	18.7	9.0
317	7.0	.0	27.8	57.8	1.6	5.8	83.4	18.3	.1	.4	19.6	32.0	17.6	12.0
329	6.8	.1	28.3	57.1	1.2	6.5	84.9	15.1	.0	.9	21.0	34.6	16.7	11.7

a/ Material obtained upon treatment with concentrated H_2SO_4.

Table 13.- Change in gas composition with synthesis reaction.

	Experiment life, hours													
	0	24	48	72	96	120	144	168	192	216	240	264	288	312
Gas contraction, percent	52.4	58.2	58.2	57.7	58.6	55.1	60.8	61.9	58.6	55.3	54.7	53.2	53.2	50.3
Synthesis gas														
Composition, volume percent														
CO_2	6.9	6.0	6.3	6.5	6.3	7.2	7.1	6.9	7.2	7.5	7.5	7.4	7.0	6.9
O_2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.2	0.1
CO	28.3	29.2	28.3	28.1	28.1	27.8	28.4	28.4	28.1	28.0	27.9	27.0	28.4	28.2
H_2	56.4	57.2	57.3	56.2	57.4	56.5	56.0	56.5	56.2	56.1	56.9	57.0	56.8	56.4
"Useful gas"	84.6	85.8	86.0	84.3	84.3	84.3	84.0	84.8	84.3	84.0	83.7	84.0	85.2	84.6
C_nH_{2n+2}	1.8	1.7	1.6	1.7	1.3	1.5	1.6	1.7	1.6	1.6	1.8	1.4	1.4	1.4
N_2	6.4	5.7	6.3	7.4	6.0	6.8	6.8	6.3	6.7	5.6	5.8	6.1	6.2	6.6
H_2:CO ratio	2.16	2.14	2.17	2.04	2.11	2.17	2.09	2.05	2.09	2.10	2.10	2.16	2.10	2.20
Product gas														
Composition, volume percent (Based on 100 mols of product gas)														
CO_2	17.4	15.2	16.0	18.1	17.2	17.1	20.7	20.7	18.7	19.1	18.7	18.2	17.4	16.4
O_2	0.1	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0
C_nH_n	.3	.5	.4	.4	.5	.4	.7	.6	.7	.7	.7	.7	.8	.9
CO	21.2	22.6	22.3	19.9	19.5	20.6	17.7	16.6	18.3	17.8	17.1	18.7	18.6	20.0
H_2	36.5	36.0	38.8	37.9	36.8	36.3	28.0	29.1	32.3	31.6	32.3	33.0	33.2	33.3
C_nH_{2n+2}	13.1	12.7	12.4	12.9	14.5	12.9	19.6	20.8	18.7	18.6	19.7	18.7	19.1	16.9
N_2	11.4	12.9	9.9	10.6	11.4	12.5	13.2	12.1	11.2	12.1	11.4	10.7	10.8	12.5
(Based on 100 mols of synthesis gas)a/														
CO_2	8.3	6.4	6.7	7.7	7.1	7.7	8.1	7.9	7.7	8.5	8.5	8.5	8.2	8.1
O_2	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_mH_n	.1	.2	.2	.2	.2	.2	.2	.2	.3	.3	.3	.3	.4	.4
CO	10.2	9.5	9.4	8.4	8.1	9.3	6.9	6.3	7.6	8.0	7.8	8.8	8.7	9.9
H_2	17.4	15.1	16.3	16.0	15.3	16.3	11.0	11.1	13.4	14.1	14.7	15.4	15.5	16.5
C_nH_{2n+2}	6.2	5.3	5.2	5.5	6.0	5.8	7.7	7.9	7.8	8.3	8.9	8.8	8.9	8.4
N_2	5.4	5.3	3.9	4.4	4.7	5.5	5.3	4.7	4.6	5.5	5.1	5.0	5.1	6.4

a/ Calculated by: (100-gas contraction)(volume-percent of product gas).

TABLE 14. - Results of small scale experiments

Experiment life, hours	Reaction temperature, °C.	Volume of gas used, l.a/	Gas velocity l./hr.	Contraction, percent	Liquid product distribution					
					Total yield, ml./m.3 synthesis gas				Yield, ml./m.3 synthesis gas	
					H_2O	Diesel oil	Gasoline	Total oil	H_2O	Total oil
0- 24............	204.5	88.1	3.7	62.5	13.1	0.6	1.9	2.5	149	28
24- 48............	206	90.4	3.8	64.6	14.8	1.9	4.1	6.0	164	66
48- 72............	206	90.0	3.8	64.6	15.1	2.0	5.0	7.0	168	78
				b/(75.1)					b/(195)	b/(91)
72- 96............	206	89.2	3.7	61.7	14.4	1.8	5.0	6.8	162	76
96-120............	206.5	87.8	3.7	57.2	13.5	1.8	4.5	6.3	154	72
120-144............	207	94.2	3.9	61.9	12.4	1.8	3.9	5.7	132	61
144-168............	210	93.3	3.9	54.3	13.8	1.4	3.8	5.2	148	56
168-192............	210.5	92.1	3.8	48.0	13.4	1.6	3.4	5.0	146	54
192-216............	211.5	93.1	3.9	48.7	12.5	1.4	2.9	4.3	134	46
216-240............	212.5	93.2	3.9	47.7	12.1	1.2	3.5	4.7	130	50
240-264............	213	94.3	3.9	52.5	11.2	1.1	3.3	4.4	119	47
264-288............	214	85.0	3.5	45.6	10.7	1.1	2.9	4.0	126	47
288-312............	215	87.4	3.6	47.8	11.4	1.0	3.5	4.5	131	52
312-336............	215	85.5	3.6	44.0	10.0	1.0	2.5	3.5	117	41
Total values........	-	1,227.8(?)	-	-	178.4	19.7	50.2	69.9	-	-
Average values......	204-215	-	3.7	55.5 b/(63.3)	-	-	-	-	145 b/(172)	57 b/(67)

a/ Corrected for temperature changes.
b/ Calculated on the basis of 100 percent H_2+CO synthesis gas.

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The following properties of the paraffin hydrocarbons, Diesel oil, and gasoline were determined: specific gravity, refractive index, iodine number, distillation curve, and acidity. The acidity of the water fraction also was determined. These results are presented in table 15.

Experimental Procedure; Iron Catalyst

Synthesis Gas Preparation

Production of components, CO and H_2. - A synthesis gas similar in composition to that used in experiment 17, employing a cobalt catalyst, was used in this test. A composition of approximately $2H_2:1CO$ was maintained; thus, its production was very similar to that previously described. A large percentage of useful gas (CO and H_2) was obtained by preparing a water-gas of approximately 37 percent CO (table 16). The hydrogen sulfide was removed, and electrolytic hydrogen was added to produce a $H_2:CO$ ratio of about 1.9:1 at a production level of 100 cubic meters per hour. Using this procedure, the average amount of useful gas in the synthesis gas was 87.2 percent.

Organic sulfur was removed from the mixed gas by passing the gas at 215° to 230° C. over a fixing agent consisting of 500 liters of copper hydroxide, diatomaceous earth, and caustic soda (20 percent copper and 3 percent caustic soda), which had been saved from experiment 17, and then passing it over 500 liters of luxmasse (10 percent copper hydroxide and 10 percent sodium carbonate). The results obtained by this purification treatment are listed in table 17 and show that throughout the whole test the sulfur content of the purified synthesis gas was less than 0.2 gm./100 m.^{3}. The equipment, procedures, and results pertaining to the manufacture and purification of the synthesis gas used in this experiment are very similar to those described experiment 17.

Table 15.- Characterization of product oil

A. Physical characteristics

	d_4^{20}	n_D^{20}	Iodine number (Odor type, pyridine method)	Distillation range, °C.					
				Initial boiling point	10 percent	50 percent	90 percent	95 percent
Total oil	0.7045	1.4018	53.5	35.0	55.0	115.5	265.0	--
Gasoline	.6808	1.3884	58.8	29.0	41.1	78.6	155.0	--
Diesel oil	.7339	1.4174	16.6	96.0	137.8	180.1	232.0	249.0

B. Product acidity

	Total acidity	Inorganic acid	Organic acid
H_2O fraction	2.92	2.75	0.17
Gasoline fraction	0.15	0.03	.12
Diesel oil fraction	.24	.10	.14
Total oil	.20	.02	.18

C. Daily characterization of product

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Gasoline														
d_4^{20}	0.6814	0.6808	0.6841	0.6871	0.6861	0.6839	0.6892	0.6885	0.6896	0.6824	0.6859	0.6845	0.6921	0.6870
n_D^{20}	1.3894	1.3885	-	1.3898	-	1.3914	1.3903	1.3910	1.3914	1.3894	1.3920	1.3906	1.3941	1.3920
Iodine No.	46.5	58.8	75.7	77.3	74.0	76.6	81.5	63.7	87.5	86.3	85.8	89.5	89.1	94.8
Diesel Oil														
d_4^{20}	0.7411	0.7404	0.7339	0.7431	0.7353	0.7422	0.7465	0.7441	0.7421	0.7433	0.7417	0.7465	0.7468	0.7491
n_D^{20}	1.4194	1.4175	1.4174	1.4165	1.4176	1.4191	1.4181	1.4176	1.4189	1.4194	1.4200	1.4208	1.4210	1.4217
Iodine No.	11.3	15.3	16.6	16.9	15.3	17.2	16.8	15.9	18.1	17.3	16.6	17.7	19.4	19.9

Table 15.- *Composition of water-gas.*

Period over which sample was taken, hr. since start of run	Gas composition, volume-percent						Sulfur content, gm./100 m.^{3}	
	CO_2	O_2	CO	H_2	CH_4	N_2	Total S	Organic S
23-25	8.8	0.0	32.8	50.6	1.2	6.6	18.1	14.8
35-37	6.8	.2	37.3	46.6	1.4	7.7	20.4	17.4
48-50	6.9	.0	37.3	46.0	1.9	7.9	23.8	21.7
58-60	6.9	.1	37.1	48.6	1.1	5.2	23.4	21.7
71-73	8.0	.0	37.8	44.9	2.4	6.9	23.4	20.6
81-83	8.2	.1	36.8	47.8	1.4	5.7	22.7	18.1
95-97	7.9	.1	37.2	47.0	1.4	6.4	--	20.9
105-108	7.3	.1	36.1	49.7	1.1	5.7	22.6	20.5
120-122	8.0	.0	36.7	48.6	0.9	5.8	48.7	22.7
129-132	8.5	.2	36.3	45.5	1.6	5.9	40.8	26.3
144-147	8.2	.1	36.7	48.1	1.4	5.5	47.8	29.5
153-155	8.5	.2	36.1	47.9	1.4	5.7	42.1	26.3
167-170	7.8	.2	37.2	47.2	1.5	6.0	47.9	29.0
177-179	8.1	.1	35.7	47.9	1.7	6.5	36.3	21.4
191-194	7.8	.1	37.3	47.9	1.6	5.3	38.3	23.6
201-203	7.7	.1	37.2	47.6	1.4	6.2	45.8	24.3
215-217	7.5	.1	38.1	47.2	1.4	5.7	42.4	36.1
225-227	7.4	.1	37.7	44.8	1.9	8.1	34.4	26.1
239-242	7.4	.1	37.5	47.4	1.9	5.7	34.7	25.6
249-252	7.4	.1	37.8	47.9	1.6	5.2	41.6	27.4
263-266	8.0	.2	36.5	49.2	1.0	5.1	44.2	27.9
273-276	7.8	.1	37.4	47.1	1.9	5.7	47.5	23.3
287-290	7.6	.2	38.1	48.6	1.1	4.5	45.6	33.0
297-299	7.6	.1	37.5	47.2	1.9	5.7	45.4	23.9
311-314	8.5	.1	36.5	48.6	1.4	4.9	52.8	28.4
321-324	7.7	.1	37.5	47.4	1.9	5.3	53.0	22.6
336-339	7.5	.1	38.3	47.6	1.6	4.9	61.4	31.3
345-347	8.1	.1	37.1	46.7	1.9	6.1	33.9	20.1
360-363	7.7	.1	38.0	48.2	1.4	5.6	67.9	32.5
369-372	6.9	.1	38.5	47.9	1.1	5.4	51.4	25.1
384-386	7.5	.1	38.2	48.0	1.4	4.8	82.3	29.3
393-395	8.0	.1	36.7	47.7	1.4	6.1	43.6	25.2
---	5.8	.1	40.6	46.0	1.1	5.4	33.0	27.7
414-416	6.0	.2	38.9	48.1	1.2	5.7	63.5	22.9
428-430	6.1	.1	38.7	45.3	1.1	7.7	34.5	30.4
438-440	6.6	.1	39.1	45.5	1.4	7.3	69.2	27.6
452-454	6.7	.2	39.0	45.6	1.0	6.5	39.0	27.3
462-464	6.3	.1	38.5	46.6	1.4	7.0	48.9	26.3
476-478	6.9	.1	39.3	46.4	1.3	6.0	58.7	24.1
486-488	7.5	.1	38.1	46.3	1.4	6.6	50.7	23.3
500-502	7.4	.1	38.1	46.8	1.1	6.5	42.0	22.9
510-512	7.4	.1	38.2	46.1	1.3	6.9	40.2	19.7
524-526	7.1	.1	38.8	46.9	1.1	6.0	62.7	27.5
534-536	7.2	.1	38.6	46.3	1.3	6.5	63.3	18.1
549-551	7.8	.1	37.9	46.7	1.1	5.4	41.1	24.9
558-560	7.9	.1	37.8	46.9	1.1	6.2	54.9	18.7
572-575	7.7	.1	38.3	48.0	1.0	4.9	79.0	28.4
582-584	7.6	.1	38.1	46.3	1.4	6.5	28.8	14.3
597-599	6.0	.1	40.2	46.2	1.1	6.4	83.8	25.0
606-608	5.8	.1	42.8	45.2	1.1	6.0	26.3	21.1

TABLE 17. - Removal of organic sulfur from synthesis gas

Period over which gas sample was taken, hour since start of run	Temperature of synthesis gas, °C.		Temperature of purifier bed, °C.	Total sulfur content of purified gas, gm./100 m.³
	Entrance	Exit		
26- 34	230	205	210-230	0.09
50- 58	230	205	210-230	.09
74- 82	230	205	210-230	.13
98-106	230	205	210-230	.09
122-130	230	205	210-230	.08
146-154	230	205	210-230	.10
170-178	230	205	210-230	.07
194-202	230	205	210-230	.11
218-225	230	205	210-230	.11
242-250	230	205	210-230	.10
270-273[a]	230	205	210-230	.10
290-292	230	205	210-230	.07
314-321	230	205	210-230	.13
339-345	230	205	210-230	.19
362-369	230	205	210-230	.15
386-394	240	210	215-230	.10
418-425[a]	240	210	215-230	.09
430-448	240	210	215-230	.11
455-473	240	210	215-230	.07
483-495	240	210	215-230	.09
503-520	240	210	215-230	.20
527-544	240	210	215-230	.14
551-568	240	210	215-230	.13
575-591	240	210	215-230	.14
599-617	240	210	215-230	.11
604-611	240	210	215-230	.13

[a] Only one value taken; other results are averages of two values.

Catalyst

A mixture of two catalysts of different copper contents was used. These catalysts were made in 35-liter batches, and the batch activities were determined. These batches were blended to form catalyst of average activity, and this mixture was placed in the converter for the test. The determination of the activity of this mixed catalyst is shown in table 18.

TABLE 18. - Determination of catalyst activity

(Catalyst composition = 350 l. of 100Fe:25Cu:2Mn: $20H_3BO_3$:$4K_2CO_3$:125 kieselguhr + 620 l. of 100Fe: 12.5Cu:2Mn:$20H_3BO_3$:$4K_2CO_3$:125 kieselguhr; reactor temperature = 240° C.; synthesis gas = $2H_2$:1CO)

Days	Gas flow, l./hr.	Operating time, hours	Contraction, percent	Liquid hydrocarbon products, cc./m.³		
				Diesel oil	Gasoline	Total
1	3.8	20	29.5	28.8	41.6	70.4
2	4.2	23	32.5	36.2	47.5	83.7
3	4.3	25	40.9	43.8	45.6	89.4
4	3.7	17	40.3	51.4	46.6	98.0

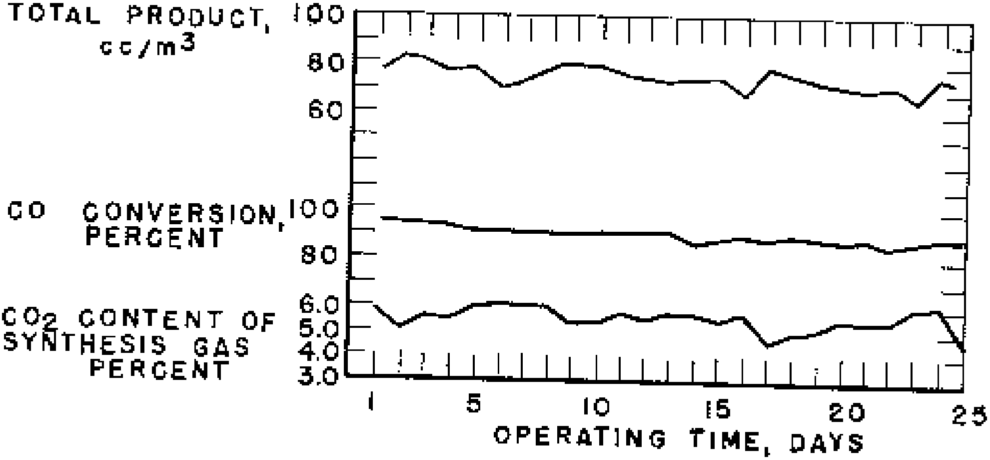

Figure 34. - Operating data for experiment No. 18.

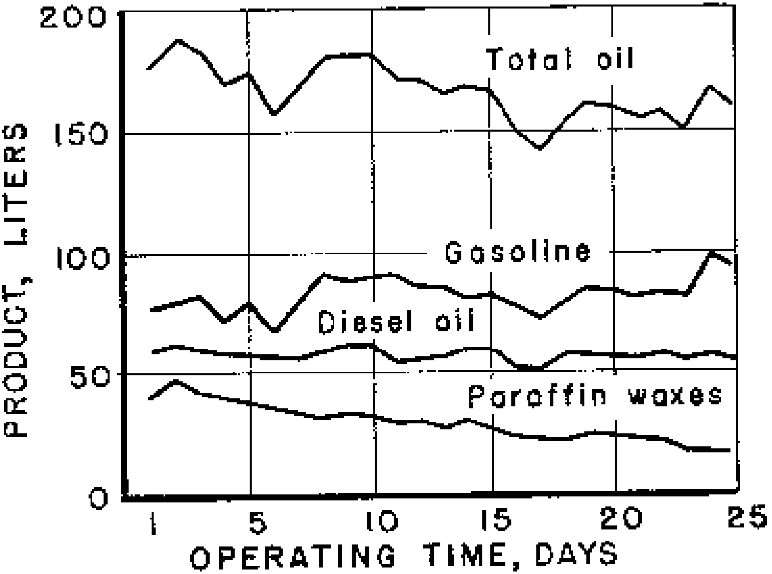

Figure 35. - Yield data for experiment No. 18.

Synthesis Operation

A reaction temperature of 250° C. was anticipated to be the best for iron catalysts, but, by increasing the hydrogen content of the synthesis gas, it was possible to lower the reaction temperature to 235° C., the temperature generally employed in this experiment. A decrease of catalyst activity also was expected with time, and a compensating increase in reaction temperature was therefore anticipated; however, actual operation at these experimental conditions resulted in very little decrease in activity, and it was possible to maintain a constant reaction temperature. To observe the effect of increased temperature, however, 238° C. was maintained for the last 3 days of the test.

Carbon dioxide is formed when iron catalysts are used in the synthesis, and the use of a synthesis gas of the same composition as the usage ratio ($0.5H_2:1CO$) results in a very short catalyst life. Using a large excess of hydrogen, however, although it decreases the reaction temperature and increases the catalyst life, is uneconomical. A compromise of these points was found in a synthesis gas ratio of $2H_2:1CO$ at a throughput of 100 $m.^3$/hr. (uncorrected for temperature and pressure), which corresponded to a gas space velocity of 100 (catalyst volume = 970 l.).

Plant operation was begun on October 7. After the temperature of the organic-sulfur remover reached the operating point, synthesis gas was passed into the converter, and the converter temperature was gradually increased. By October 8, the hot water temperature had reached 235° C., and 22-percent contraction was achieved, indicating that the reduction of the catalyst had been completed. On the 9th of October, starting at 10 o'clock, data were recorded every 24 hours until 3 o'clock, October 25, when a welded section of a cooling pipe in the converter developed a leak, allowing the hot water to leak into the synthesis chamber and interrupted the run. Repairs were completed the morning of October 27, and the test was resumed; by 1 o'clock on October 28, normal operating conditions were regained. The test continued in a normal manner at a constant temperature of 235° C. with no significant decrease in catalyst activity. During the last 3 days of the experiment, the operating temperature was increased to 238° C. to observe any effect on synthesis operations. The results of this experiment are given in table 19 and figures 34 and 35. The variation in temperature throughout the catalyst bed is shown in table 20, and the change in gas composition as a result of the synthesis reaction is given in table 21. As a reference, the results obtained from a small-scale experiment (flow rate = ½ l./hr.) using the same synthesis gas composition are given in table 22. In all cases, operating time was computed from October 9, and October 25, 26, and 27 were not figured in the total life of the test. The characteristics of the product oil are presented in table 23.

TABLE 19. - Operating conditions and product yields, experiment 18

Operating conditions					Daily product yields								
Time, days	Temp., °C.	Flow of synthesis gas[a/]		Contraction, percent	H_2O		Wax, l.	Diesel oil, l.	Gasoline, l.	Liquid + solids		Gasol	
		m.3/day	m.3/hr.		l.	cc./m.3[b/]				l.	cc.m.3[b/]	m.3	l./m.3[b/]
1	235	2,299	95.6	23.7	36	16	41	60	77	178	77	7.3	3.2
2	235	2,274	94.7	25.0	44	19	48	62	79	189	83 c/(94.5)	6.5	2.9
3	235	2,265	94.4	24.3	37	16	42	60	82	184	81	7.0	3.1
4	235	2,215	92.3	24.4	40	18	40	58	72	170	77	7.0	3.2
5	235	2,234	93.1	23.5	32	13	37	58	80	175	78	6.5	2.9
6	235	2,244	93.5	23.9	28	12	36	56	66	158	70	6.5	2.9
7	235	2,316	96.5	23.2	31	13	34	56	80	170	73	7.0	3.0
8	235	2,330	97.1	23.6	28	12	32	59	91	182	78	6.0	2.6
9	235	2,299	95.8	24.4	17	7	33	62	88	183	80	6.5	2.8
10	235	2,311	96.3	23.6	25	11	32	61	90	183	79	7.0	3.0
11	235	2,282	95.1	23.0	29	13	29	55	90	174	76	6.5	2.9
12	235	2,326	96.9	22.9	27	12	30	56	86	172	74	6.5	2.8
13	235	2,307	96.2	23.1	29	13	27	56	85	168	73	6.5	2.8
14	235	2,305	96.1	23.0	26	11	30	59	81	170	74	6.0	2.6
15	235	2,265	94.4	22.8	28	12	27	59	82	168	74	6.5	2.9
16	235	2,270	94.6	22.2	25	11	23	52	77	152	67	6.0	2.6
17	235	1,835	87.4	24.6	30	16	22	51	71	144	79	6.0	3.3
18	235	2,078	86.6	24.3	25	12	22	57	77	156	75	6.5	3.1
19	235	2,240	93.3	24.6	29	13	24	56	84	164	73	6.0	2.7
20	235	2,268	94.5	24.5	25	11	24	55	83	162	71	6.0	2.6
21	235	2,246	93.6	24.4	28	12	22	55	80	157	70	7.0	3.1
22	235	2,249	93.7	24.5	25	11	21	57	82	160	71	5.5	2.4
23	238	2,288	95.3	24.9	29	13	17	55	80	152	66	7.0	3.1
24	238	2,270	94.6	25.8	25	11	16	57	97	170	75	6.5	2.9
25	238	2,239	93.3	24.5	27	13	16	54	92	162	73	6.0	2.7
Average	235		94.2	23.9		13					c/ 75 (86)		2.9
Total		56,255			725		725	1,426	2,052	4,203		161.8	

a/ Gas-meter values corrected and reduced to standard conditions.
b/ Per cubic meter of inlet gas.
c/ Values within parenthesis have been corrected for the inerts content of the feed gas.

TABLE 20. Temperature variation in synthesis converter.

Time, days	Heating jacket, °C.		Catalyst bed, °C.									Synthesis gas	
	Inlet	Outlet	1	2	3	4	5	6	7	8	9	Flow m.^{3}/hr.	Contraction, percent
0..........	235	235	234	234	235	235	235	239	235	233	234	108.2	27.0
1..........	235	236	234	235	234	235	235	238	235	234	233	100.9	25.3
2..........	235	236	234.5	234.5	235	235	235	237	235	233	233	102.8	26.1
3..........	235	236	234	234	235	234.5	235	238	234.5	232	233	103.1	24.9
4..........	235	236.5	235	235	235	235	235.5	237	235.5	233.5	233.5	102.1	24.1
5..........	235	236	235	235	236	235	236.5	237	235	234	234	106.5	22.9
6..........	235	236	235	235	235	234.5	235	237.5	234.5	233	233	103.6	23.5
7..........	235	236	234.5	234.5	235	233	234.5	237	234.5	233	233	93.9	25.3
8..........	235	236	235	234.5	235	234.5	235	237.5	235	233	233	105.4	23.3
9..........	235	236	235.5	235	235.5	234	235.5	238	235	233.5	233.5	95.0	24.3
10..........	235	236.5	234	234	234	233	234	238	234	232	233	104.4	22.9
11..........	235	236.5	234	234	234	233	234	238	234	232	232	98.8	22.7
12..........	235	237	234.5	234	234	233	234	238	234	232	232.5	108.4	22.9
13..........	235	236.5	234.5	234	234	233	234.5	238	234	232	232.5	102.8	23.4
14..........	235	236	235	234	234	233	235	238	234.5	233	234	103.9	23.7
15..........	235	236	235	235	234	233.5	235	238	234	233.5	233	98.5	22.4
16..........	235	236	235	235	235	233.5	234	238	234.5	232	233.5	100.9	21.5
17..........	235	234	234.5	234	233	231.5	233.5	236	233.5	231.5	231.5	101.4	24.7
18..........	235	234	234.5	234	234	231.5	233.5	233.5	233	232	232	98.9	23.7
19..........	235	234	232.5	231	231.5	229	231	235	234	229.5	230.5	101.7	24.5
20..........	235	234	233.5	233	233	230.5	233.5	236	234	230.5	231	101.4	25.2
21..........	235	234	233	233	233	230	233	235	234	231	231	99.2	23.8
22..........	235	234	232	232	232	229	231	235.5	232	230	230	100.4	24.0
23..........	238	237.5	234	234	234	232	233	238	234	232	231	102.6	25.0
24..........	238	237.5	234	234	234	232	234	239	234	232	232	99.3	25.6
25..........	238	237.5	234	234	234	232	234	238.5	234	232	233	96.3	24.2

Table 21.– Change in gas compositions during synthesis.

	Operating time, days																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Gas contraction, %	23.7	25.0	31.5	25.1	23.5	23.9	23.2	23.5	24.4	23.5	23.0	22.9	23.1	23.0	22.8	22.2	24.6	24.3	24.6	24.5	24.4	24.5	24.9	25.8	24.5
CO conversion, %	93.8	94.4	93.2	92.6	91.3	91.3	90.9	90.7	90.0	90.7	90.7	92.0	89.1	86.4	88.1	89.0	87.9	89.1	88.0	87.0	86.3	85.4	87.3	87.5	87.7
Synthesis gas																									
Composition, vol. %																									
CO_2	5.9	5.1	5.6	5.5	6.0	6.1	6.0	6.0	5.3	5.3	5.7	5.5	5.7	5.7	5.4	5.7	4.5	4.9	5.1	5.5	5.4	5.4	6.0	6.1	4.5
O_2	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1
CO	29.4	30.1	29.3	29.7	30.0	29.9	29.6	29.6	29.9	30.1	30.2	30.3	30.1	30.2	31.0	30.1	30.7	30.3	30.0	29.9	30.0	30.1	30.0	30.4	30.8
H_2	57.0	57.8	58.0	57.9	56.2	56.1	56.2	56.7	57.1	56.9	57.1	57.0	56.8	58.0	57.9	57.3	57.0	57.4	57.3	56.9	56.9	57.9	57.0	57.0	57.6
Useful gas	86.4	87.9	87.3	87.6	86.2	86.0	85.8	86.3	87.0	87.0	87.3	87.3	86.9	88.2	88.9	87.4	87.7	87.7	87.3	86.8	86.9	88.0	87.0	87.4	88.4
CH_4	1.4	1.3	1.4	1.5	1.6	1.3	1.5	1.5	1.6	1.9	1.6	1.7	1.7	1.4	1.6	1.5	1.5	1.4	1.6	1.5	1.5	1.2	1.4	1.3	1.3
N_2	5.2	5.7	5.6	5.3	6.2	6.5	6.6	6.1	6.0	5.7	5.3	5.4	5.6	4.6	4.0	5.3	6.2	5.9	5.9	6.2	6.1	5.3	5.5	5.2	5.7
H_2:CO ratio	.48	.52	.50	.51	.48	.55	.49	.50	.57	.52	.49	.48	.57	.50	.46	.46	.54	.50	.53	.53	.51	.53	.55	.57	.53
Product gas																									
Composition, vol. %																									
(Based on 100 mols of product gas)																									
CO_2	25.8	26.5	26.3	26.5	27.5	26.5	26.2	26.4	26.6	25.3	25.7	25.6	26.0	24.8	25.6	25.6	24.8	24.6	24.1	24.7	23.4	24.3	25.5	25.6	24.4
O_2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C_nH_m[a]	.6	.7	1.0	.7	1.0	1.3	1.1	.9	.9	.9	.9	.9	1.1	.8	1.1	1.1	.9	1.0	1.0	.9	.8	1.3	.7	.9	1.0
CO	2.3	2.3	2.6	2.9	3.4	3.4	3.5	3.5	4.0	3.7	3.7	4.1	4.2	5.3	4.7	4.2	4.9	4.4	4.8	5.1	4.6	5.8	5.0	5.1	5.1
H_2	57.4	57.4	57.8	58.1	56.3	57.3	57.3	56.2	55.3	56.1	56.6	57.1	56.8	58.5	57.9	57.2	56.3	57.1	57.3	56.8	57.3	56.8	56.3	56.4	57.4
CH_4	4.0	4.7	4.3	4.2	4.6	4.2	3.8	5.6	5.4	5.7	5.7	5.5	5.3	4.1	4.7	4.8	5.1	5.3	4.9	5.0	5.7	5.0	5.0	5.0	5.0
N_2	8.8	8.3	7.9	7.6	7.1	7.5	8.1	7.2	7.6	7.2	7.1	6.6	6.5	6.3	5.9	7.0	8.1	7.5	7.8	7.4	7.3	6.7	7.4	6.9	7.0
(Based on 100 mols of synthesis gas)[b]																									
CO_2	19.8	19.9	14.5	20.2	21.0	20.2	20.2	20.2	20.1	20.1	19.8	19.7	20.0	19.1	19.8	19.9	18.7	18.6	18.2	18.7	18.4	18.3	19.1	19.0	18.4
O_2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C_nH_m[a]	.5	.5	.8	.5	.8	.8	.8	.7	.7	.7	.7	.7	.8	.6	.8	.9	.7	.8	.8	.7	.6	1.0	.5	.7	.8
CO	1.8	1.7	2.0	2.2	2.6	2.6	2.7	2.7	3.0	2.8	2.8	3.2	3.2	4.1	3.6	3.3	3.7	3.3	3.6	3.9	3.5	4.4	3.8	3.8	3.8
H_2	43.8	43.1	43.7	42.0	43.2	43.7	43.9	43.0	41.7	42.8	43.6	44.0	43.7	45.0	44.7	44.5	42.3	43.2	43.2	42.9	43.3	42.8	42.3	41.8	43.3
CH_4	3.0	3.5	3.3	3.1	3.5	3.2	2.9	4.3	4.1	4.4	4.4	4.2	4.1	3.2	3.6	3.7	3.8	4.0	3.7	3.8	4.3	3.8	3.8	3.7	3.8
N_2	6.7	6.2	5.9	5.7	5.4	5.6	6.2	5.9	5.8	5.5	5.5	5.1	5.0	4.8	4.6	5.4	6.1	5.7	5.9	5.6	5.4	5.1	5.6	5.1	5.3

[a] High-molecular-weight hydrocarbons; obtained upon treatment with conc. H_2SO_4.

[b] Calculated by (volume percent of product gas) × (100 − gas contractions).

TABLE 22. - Small-scale test under comparable conditions

Time, days	Temperature, °C.	Synthesis gas		Liquid products					
		Flow l./hr.	Contraction, percent	H_2O		Diesel oil, cc.	Light oil, cc.	Total oil	
				cc.	cc./$m.^3$ [a]			cc.	cc./$m.^3$ [a]
1..........	235	92.5	32.9	2.3	25	2.6	4.1	6.7	73
2..........	235	92.4	34.8	2.4	26	3.0	3.7	6.7	73
3..........	235	96.5	33.8	2.6	27	2.8	4.3	7.1	74
4..........	235	90.9	35.0	2.3	26	2.3	4.4	6.7	74
5..........	235	95.0	32.9	2.4	25	2.4	4.0	6.4	67
6..........	235	96.2	34.3	2.4	25	2.7	3.8	6.5	68
7..........	235	90.0	35.2	2.4	27	2.4	3.6	6.0	67
8..........	235	96.8	35.8	2.5	26	2.5	3.5	6.0	62
9..........	235	93.0	36.4	1.1	12	2.9	3.7	6.6	71
10..........	235	91.1	35.9	1.2	13	2.4	3.8	6.2	67
11..........	235	87.6	33.7	1.5	17	1.9	3.8	5.7	65
12..........	235	91.3	34.4	1.0	11	2.2	3.9	6.1	67
13..........	235	94.6	35.8	1.2	13	2.2	3.6	5.8	61
14..........	235	95.4	34.1	2.0	21	2.6	4.2	6.8	71
15..........	235	89.7	33.4	1.0	11	2.3	4.1	6.4	71
16..........	235	92.5	31.5	.9	10	2.2	3.7	5.9	64
17..........	235	94.1	31.6	2.3	24	2.0	3.8	5.8	62
18..........	235	93.2	32.7	2.2	24	1.9	3.4	5.3	57
19..........	235	92.1	31.9	2.4	26	2.0	3.4	5.4	59
20..........	235	90.4	32.9	2.3	26	1.7	3.7	5.4	60
21..........	235	90.6	31.5	1.1	12	2.0	3.9	5.9	65
22..........	235	87.7	38.0	1.1	13	1.9	3.7	5.6	64
23..........	238	90.0	33.0	1.2	13	1.5	3.8	5.3	59
24..........	238	89.8	32.5	1.2	14	1.9	3.7	5.5	62
25..........	238	92.6	31.9	1.1	12	1.4	4.2	5.6	60

[a] Per cubic meter of synthesis gas.

TABLE 23. - Characterization of products

A. Physical characteristics of product oil

Component	Specific gravity, d_4^{20}	Refractive index, n_D^{20}	Iodine number	Total acid number
Gasoline..............	0.6896	1.3980	167	-
Diesel oil............	.7526	1.4270	60	-
Total oil.............	.7301	1.4178	138	0.10

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B. Distillation of product oil

Component	Distillation range, °C.						Percent distilled up to		
	Initial b.p.	10%	50%	80%	95%	End point	150°C.	200°C.	220°
Gasoline....	40.0	58.0	92.8	124.5	172.0	206.0	90.0	97.2	
Diesel oil..	102.0	154.0	205.0	242.5	282.0	-	7.6	46.0	63.4
Total oil...	39.5	68.1	156.0	278.5	-	-	47.2	61.9	66.9

C. Analysis of gasol

Time, days	Composition, percent							
	CO_2	O_2	CO	H_2 a/	C_3+ b/	C_2H_4 c/	C_nH_{2n+2} d/	n
12..................	48.4	0.3	0.7	3.3	29.1	7.5	5.8	3.2
16..................	40.3	1.0	2.0	6.4	21.0	5.7	15.3	1.2
18..................	36.4	1.0	2.0	3.1	26.2	5.3	21.7	1.6

a/ Determined by adsorption with silver permanganate.
b/ Determined by use of 88 percent H_2SO_4.
c/ Determined by adding 102-percent H_2SO_4 to 0.5-percent Ag_2SO_4.
d/ Determined by bomb method.

Discussion of Results

A study of the product yield data reveals that a maximum oil production (189 l./day; 83 cm.³/m.³) was reached on the second day. The daily average yield of oil then decreased slowly. Raising the reaction temperature to 238° C. during the last 3 days produced no significant increase in oil yield. These results indicate that a constant operating temperature may be maintained for at least a month when iron catalysts are used under these conditions in the hydrocarbon synthesis. No conclusions may be drawn concerning catalyst life, specific loss of activity, or effect of operating temperature without additional data and longer tests. Because it is known, however, that iron catalysts may be used effectively at temperatures up to 260° C., it may be predicted that, by slowly increasing the operating temperature as needed, a catalyst life long enough to satisfy economic requirements on a commercial scale may be obtained.

In order to increase the catalyst life, a synthesis gas containing about $2H_2$:1CO was used. Accordingly, about 57 percent H_2 remained in the product gas, whereas about 90 percent of the CO was consumed, leaving only 2 to 6 percent of CO in the product gas. No significant increase in oil production may be obtained, therefore, until a synthesis gas richer in CO is used. The usage ratio obtained in this experiment was $0.5H_2$:1CO (see table 21).

Figure 23 shows that although the CO_2 content of the synthesis gas is small it varies inversely with the yield of oil subsequently obtained. This suggests the advisability of removing CO_2 from the synthesis gas before it passes through the reactor.

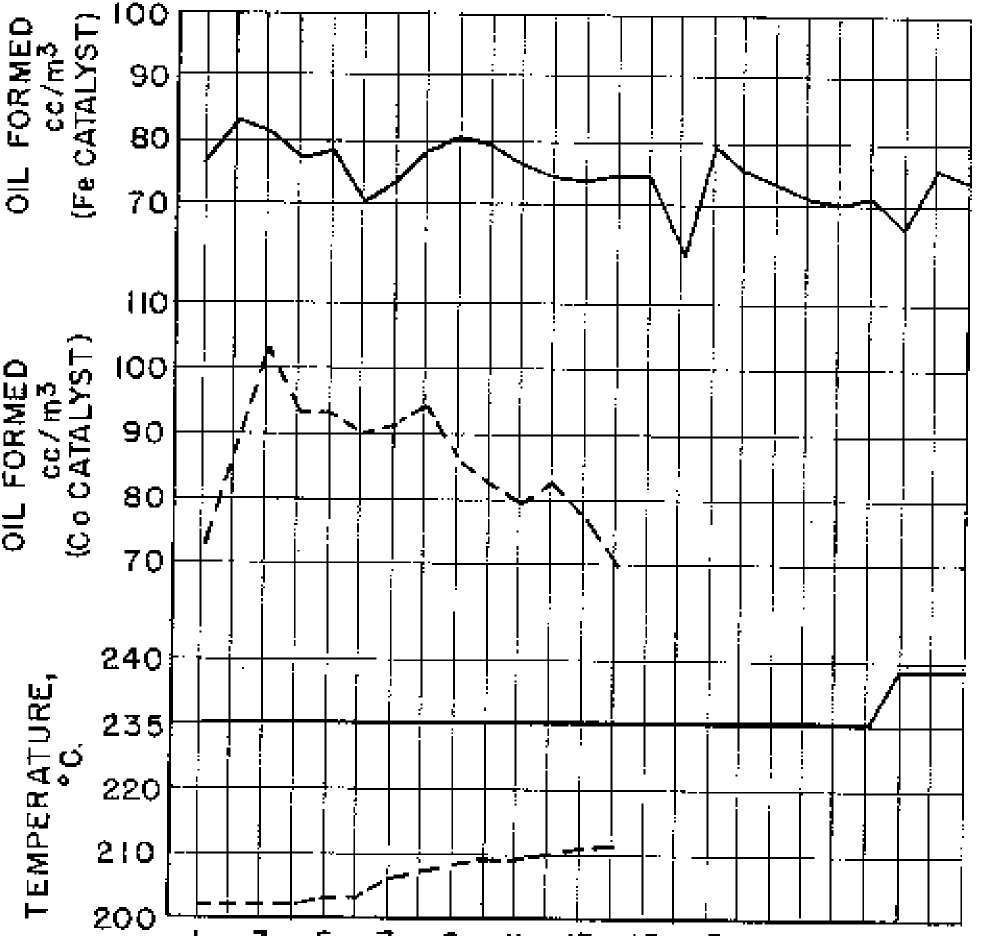

Figure 36. - Co and Fe catalysts; experimental results.

When the production of oil is calculated on the basis of the useful gas (the sum of $CO + H_2$) in the synthesis gas mixture (excluding CO_2, CH_4, and N_2), a value of 94.5 cm.^{3}/m.^{3} of useful gas is obtained, which compares favorably with those results obtained in a laboratory-scale activity test. The average oil production for the entire test is 75 cm.^{3}/m.^{3} of inlet gas; on the basis of useful gas, this value becomes 86 cm.^{3}/m.^{3}. On the basis of a cubic meter of $CO + H_2$ consumed, the oil production is 180 cc./m.^{3}; this compares favorably with the corresponding value (139 cm.^{3}/m.^{3}) obtained for cobalt catalysts.

Table 23 shows that 67 percent of the total oil produced distills up to 220° C.; 78 percent of the total oil was obtained as a distillate up to 270° C. It is interesting to note the high degree of unsaturation; that is, the iodine number of the total oil is 138, and that of the light oil stripped from the active carbon adsorbers was 167. Figure 35 indicates a tendency toward lower-molecular-weight products as the synthesis progresses. Comparison of the synthesis oil formed by cobalt catalyst to that formed by iron catalyst shows that the latter has a larger unsaturates content and larger fraction of high-boiling constituents.

Comparison of the results of the two-week test (July 1940) with cobalt catalyst with those obtained from iron catalysts is given in table 24 and plotted in figure 36.

TABLE 24. - Comparison of results obtained during synthesis with cobalt and with iron catalysts

	Cobalt	Iron
Operating time, days	14	25
Initial temperature, °C.	202	235
Final temperature, °C.	211	238
Total amount of synthesis gas used, m.^{3}	26,729	56,255
Total oil formed:		
Liters	2,288	4,203
cc./m.^{3} of synthesis gas	86	75
cc./m.^{3} of useful gas	102	86
cc./m.^{3} of H_2+CO reacted	139	180

When the iron catalyst was used in laboratory-scale tests, no formation of water was noticed; in a large-scale test such as this, however, water was detected in the product. Moreover, in this test, possibly due to the low reaction temperature, gasol formation was small, averaging 3 l./m.^{3} of synthesis gas (table 19). The composition of the gasol fraction is given in table 23-B.

Thus, there seems to be justification for using iron catalysts industrially, but because a synthesis gas is used that differs in composition from the theoretical, the exit gas has the following average percentage composition: $CO_2 = 25.7$, $O_2 = 0.1$, $C_mH_n = 1.0$, $CO = 4.1$, $H_2 = 56.7$, $CH_4 = 4.9$, and $N_2 = 7.5$. A method of recirculating this tail gas would greatly improve the efficiency. For this purpose, a simple flow sheet is proposed in figure 37, in which, first, the CO_2 is removed from the waste gas, and, second, the hydrogen is recirculated after passing through the condenser. The CO_2 removed from the tail gas could be reacted with the methane in coal gas in a special CO generator; the reduction of CO_2 by means of coke is not economically sound because of the high temperature (combustion with O_2) required. The CO formed by reaction with coal gas is then mixed with the recirculating H_2 to form additional synthesis gas. By this procedure with iron catalyst, 7.5 l. of synthesis gasoline and 8.4 kg. of coke could be produced from 50 kg. of coal.

CALCULATION OF HEAT TRANSFER DATA

The types of calculations employed in determining the heat-transfer characteristics of the various convertors studied are exemplified by those shown below for a 24-hour period (July 22-July 23) during operation of the 100-m.^{3}/hr. water-cooled converter using a cobalt catalyst.

Based on the average composition of the synthesis gas (table 6) as well as the average extent of reaction and analysis of the product gases (table 9) for that 24-hour period, a value for the heat of reaction of 7,854 kcal./mol was obtained. Reduced to one cubic meter of synthesis gas, this value becomes 350 kcal., and, at the throughput of 1,865 m.^{3} during this time, the heat generated in the converter was calculated to be

$$\frac{350 \times 1,865}{24} = 27,200 \text{ kcal./hr.}$$

From table 10, the average temperature differential between cooling medium and catalyst bed was observed to be 4.8° C.; the cooling surface available in this converter was 139.05 m.^{2}. From these data, the over-all coefficient of heat transfer could be obtained; thus

$$U = \frac{27,200}{4.8 \times 139.05} = 40.75 \text{ (kcal.)(m.}^2)^{-1}\text{(hr.)}^{-1}\text{(C.)}^{-1}.$$

In these calculations, the heat of reaction was divided by the average difference in temperature, a situation not at all representative of actual conditions in the converter, as the reaction does not proceed in a uniform manner throughout the bed but is concentrated in that portion of the catalyst nearest the gas inlet. Actual calculations of such point-to-point conditions, however, would prove extremely complicated.

Where heat is transferred, as it is in this case, through a gas film, an intervening metal wall, and a liquid film, by far the greatest resistance to the heat flow is offered by the gas film. Thus, the over-all coefficient of heat transfer obtained above may be assumed to approximate that of the heat-transfer coefficient existing across the gas film. In designing the 100-m.^{3}/hr. converter, some estimates were made of the gas film coefficient. How well these estimates were substantiated by subsequent experimental evidence will be discussed below.

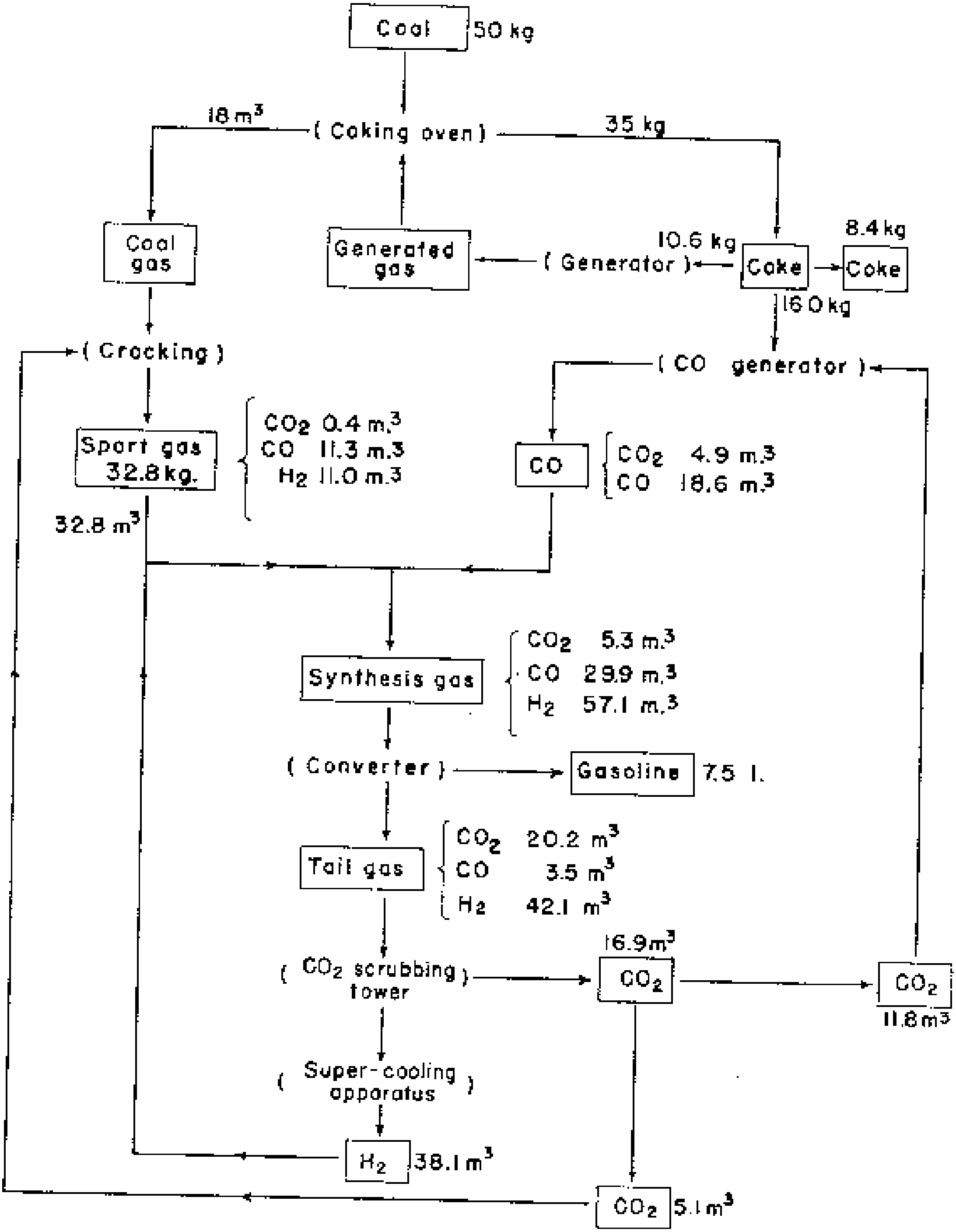

Figure 37. - Proposed flow diagram for recirculating tail gas.

Although the 100-m.^{3}/hr. converter utilizes the cooling medium inside tubes while the reaction gases flow around the outside of the tubes, estimates of the film coefficients were made on the basis of an inner-catalyst converter (gases inside tubes; coolant outside tubes) containing four 25-mm. I.D. tubes, such as the converter shown in figure 2. This was done to simplify the necessary calculations. Assuming a constant hourly flow of gases through the tubes as 100 liters at 200° C., the gas velocity within the catalyst tubes is given by

$$\frac{(100)\ (1{,}000)(4)(473)}{(2.5)^2(\pi)(3{,}600)(4)(273)} = 2.45 \text{ cm./sec.}$$

Of course, the volume of the gases is reduced in their passage through the tubes because of the reactions occurring, but this effect has been disregarded. The resulting velocity (2.45 cm./sec.) is much lower than that usually used in industry and gives rise to a Reynolds number of

$$\frac{(2.5)(0.316)(2.45)}{(1{,}000)(2{,}351)(10)^{-7}} = 3.3$$

which suggests that a reasonable estimate might be made by assuming that heat is transferred through the gas only by convection in an empty tube. The Grashof and Prandtl numbers were calculated as

$$N_{Gr} = \frac{L^3 \rho^2 \beta g \Delta t}{\mu^2} = 212.0$$

and

$$N_{Pr} = \frac{c\mu}{k} = 0.436$$

by using the following values:

L = inside diameter of catalyst tube = 25 cm.

ρ = density of the gas = 0.000316 gm./cm.^{3}

β = coefficient of expansion of the gas = $\frac{1}{273}$ °C.$^{-1}$

g = acceleration due to gravity = 980 cm./sec.^{2}

Δt = temperature difference between gases and cooling surface = 2°C.

μ = gas viscosity = 2,351 x 10^{-7} poise

c = specific heat at constant pressure = 0.578 cal./gm.

k = specific thermal conductivity = $\frac{0.112}{360}\ \frac{\text{cal.}}{\text{sec. °C.}}$

Thus,

$$\log (N_{Gr})(N_{Pr}) = 1.9626$$

and, from the diagram on page 156 of Uchida's book,

$$\log \frac{hd}{k} = 0.34,$$

yielding the film coefficient

$$h = (1.22)\ \frac{(2.19)(0.112)}{(2.5)} = 11.68\ (\text{kcal})(\text{m.}^2)^{-1}(\text{hr.})^{-1}(^\circ\text{C.})^{-1}$$

where 1.22 is the coefficient for erect pipes.

It is evident, therefore, that the over-all heat-transfer coefficient (U = 40.75) is much greater than the gas film coefficient, h, calculated for heat transfer only by free convection. It is believed that this difference in coefficients is a result of (1) the effect of turbulence caused by the flow of gases around the catalyst granules in the packed tubes and (2) existence of a partial liquid film inside the catalyst tube resulting from formation of liquid products in the synthesis.

Application of an equation developed by A. P. Colburn for calculating the gas film coefficient in tubes for turbulent flow at the critical velocity resulted in a value even smaller:

$$h = 8\ aC_pZ^{0.2}G^{0.83} = 4.10\ (\text{kcal.})(\text{m.}^2)^{-1}(\text{hr.})^{-1}(^\circ\text{C.})^{-1}$$

where

h = gas film coefficient of heat transfer

a = constant depending on size of pipe

C_p = specific heat of gas at constant pressure = 0.578 (kcal.)(kg.)$^{-1}$(°C.)$^{-1}$

Z = viscosity of gas = 2,351 x 10^{-5} centipoise

G = mass velocity of gas = 0.000316 x 2.45 (gm.)(cm.)$^{-2}$(sec.)$^{-1}$

It is obvious that Colburn's equation does not apply in this case and demonstrates the importance of the state of gas flow in the selection of a suitable method of film coefficient calculation.

SUMMARY

1. Using a cobalt catalyst in a water-cooled converter (designed for synthesis gas throughput of 100 m.^{3}/hr.), a 2-week run was carried out successfully.

2. Over a reaction temperature range of 200° to 215° C. and at an average gas throughput of 79.6 m. /hr., the following average yields were obtained at an average apparent contraction of 56.2 percent: 168 ml. of water, 86 ml. of primary liquid products (oil), and 7 liters of gasol per cubic meter of synthesis gas. Correcting these results for the 15.5 percent of inerts contained in the synthesis gas produced an actual contraction of 66.5 percent and increased the yield values to 199 ml. of water, 102 ml. of oil, and 8 liters of gasol per cubic meter of pure $2H_2$:1CO gas.

3. These results suggest that commercial synthesis of gasoline and hydrocarbon oils in a water-cooled converter may be economically feasible.

4. Using the 100 m.3/hr. converter and an iron catalyst, a continuous run of one month was conducted.

5. No significant decrease of catalyst activity was noted over a period of one month using a synthesis gas of $CO:H_2=1:2$.

6. The average amount of oil formed was 75 cc./m.3 of synthesis gas (on basis of useful gas, 86 cc./m.3); this compares favorably with the corresponding yields using cobalt catalyst.

7. The product oil rich in unsaturated compounds.

8. If iron catalyst is used with a hydrogen-rich feed gas, the H_2 in the exit gas must be recirculated for maximum efficiency.

9. Comparison of the results of the synthesis of hydrocarbons in various converters having different ratios of cooling surface to catalyst volume (A/V) it was possible to determine the optimum A/V for use in future designs. The results are compared in table 25. It is evident from these data that locating the catalyst outside the cooling tubes is preferable, as less cooling surface is thus required. (The number of plus signs in the right-hand column of table 25 indicates the merit of the furnace.) The table shows that the best arrangement tested was that of an outer-catalyst converter where a cooling surface of 1.32 cm.^{2} was present for every cubic centimeter of catalyst.

TABLE 25. - Comparison of cooling surface areas of various converter designs

Type of converter	Throughput, m.3/hr.	Coolant	Tube I.D., mm.	Center-to-center spacing of tubes, mm.	A/V	Measure of merit, (-)<(0)<(+)
Inner-catalyst....	(100 l.)	Oil	55	-	0.728	-
Do.	(100 l.)	do.	35.7	-	1.120	0
Do.	(100 l.)	do.	25.0	-	1.600	+++
Outer-catalyst....	3	Water	-	48 x 42	.963	+
Do.	10	do.	-	45 x 39	1.261	++
Do.	6	do.	-	42.5 x 36.2	1.345	+++
Do.	100	do.	-	42.5 x 36.8	1.322	+++