Table 3.8

Experimental Conditions[1] for Run 5

Experiment	H_2/CO	SV, V/V/h	T, °C	P, kPa	Time, h
5-1	1.61	200	250	1000	4.2
5-2	1.55	250	250	1000	3.6
5-3	1.03	200	250	1000	4.0
5-4	1.60	250	260	1000	3.6
5-5	1.55	250	270	1000	3.8
5-6	1.96	250	250	1000	3.5
5-7	1.51	250	230	1000	3.5
5-8	1.46	250	240	1000	3.9
5-9	1.55	100	240	1000	4.5
5-10	1.49	250	240	1550	3.5
5-11	1.51	250	240	2275	4.7
5-12	1.49	250	240	500	4.6

3.2.3 Results and Discussion

The following reactions have been assumed to take place during hydrocarbon synthesis:

1a. $(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$ Paraffins

1b. $2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$ Olefins

2a. $(n+1)H_2 + 2nCO \rightarrow C_nH_{2n+2} + nCO_2$ Paraffins

2b. $nH_2 + 2nCO \rightarrow C_nH_{2n} + nCO_2$ Olefins

3a. $H_2O + CO \rightleftarrows CO_2 + H_2$ Water-gas shift reaction

3b. $2CO \rightarrow CO_2 + C$ Boudouard reaction

Previous investigators (16, 55, 56, 57) have postulated that H_2O is the primary oxygenated product, that reactions 2a and 2b are not important, and that CO_2 is formed primarily via reaction 3a. Recently, Dry and coworkers (25) found that, on a fused iron catalyst, a nine-fold increase in the gas flow rate had no effect on overall activity (i.e. moles of $H_2O + CO_2$ produced) but led to a decrease in the relative amount of CO_2 to H_2O produced. As a lower residence time should increase the ratio of primary to secondary products, Dry et al. (25) postulated that CO_2 was produced via a secondary reaction.

---

[1] Accurate experimental conditions for each reactor and detailed results are given in the tables for run 5 in Appendix D, pages 142 to 154.

In all our experiments, except those conducted at low temperature (Experiment 5-7) and low pressure (Experiment 5-12), CO conversion was greater than 95%, whereas H_2 conversion rarely exceeded 70%. Approximately 30 to 40% of the exit gas was CO_2. With the help of the results given in Appendix D it can be shown that reactions 1a, 1b and 3a are the most probable reactions taking place. As an example we will use the results from reactor 5 in Experiment 5-1.

Let us assume that reactions 1a and 1b are the primary reactions.

Then, H_2 consumed, μmol/min, to:

$$CH_4 = 3 \times 135.9 = 407.7$$

$$C_2H_6 = 2.5 \times 125 = 312.5$$

$$C_2H_4 = 2 \times 14.7 = 29.4$$

$$C_3H_8 = 2.33 \times 48.9 = 114.0$$

$$C_3H_6 = 2 \times 131.6 = 263.2$$

$$C_4H_{10} = 2.25 \times 34.3 = 77.1$$

$$C_4H_8 = 2 \times 70.2 = 140.1$$

$$C_5{+} = 2 \times 790.4 = 1580.8$$

Total H_2 consumed to form hydrocarbons = 2925.0 μmol/min.

Assuming that reaction 3a is the only source of CO_2 production the amount of H_2 produced via the shift reaction is 652.4 μmol/min.

Therefore, the overall H_2 conversion should be

$$= 2925.0 - 652.4 = 2272.6 \ \mu\text{mol/min}$$

The above calculated value is only 1% higher than the observed result of 2296.9 mol/min. Such good agreement between calculated and observed values is true for most of our results, and this ratifies our assumption that reactions 1a and 1b are the primary FT reactions and CO_2 is produced mainly via reaction 3a. In a few cases the calculated value is as much as 20% higher than the observed result; whether this is due to experimental errors or a small amount of CO_2 being produced via reaction 3b cannot be elucidated at present.

There is no agreement between calculated and observed values if we assume reactions 2a and 2b to be the primary reactions. It is, however, not possible to show via such calculations whether reactions 1a, 1b, 2a, and 2b take place together to produce hydrocarbons, water, and CO_2 without the occurrence of the shift reaction. But, our calculations do substantiate the postulates of past researchers (16, 25, 55, 56, 57) whose inferences, that reactions 1a and 1b are primary reactions and that CO_2 is formed via the water-gas shift reaction, were based mainly on experimental observation.

It is important to compare H_2 and CO conversions and selectivity to C_5+ hydrocarbons on sulfided and unsulfided catalysts. Table 3.9 shows some typical values for the catalyst with 0.4 wt % S (reactor 4) and the catalyst without sulfur (reactor 5).

Table 3.9

Conversion of H_2 and CO on Precipitated Iron-based Catalyst

H_2/CO = 1.5 ± 2%, SV = 245 V/V/h ± 5%

	Total Hydrogen Converted, %		Total Carbon Monoxide Converted, %	
Reactor	4	5	4	5
Nominal S, wt %	0.4	0	0.4	0
T = 250°C, P = 1000 kPa	64	62	99(43)	99(36)
T = 230°C, P = 1000 kPa	31	29	72(40)	72(40)
T = 242°C, P = 500 kPa	32	31	71(39)	72(39)

( ) = selectivity, % CO converted to C_5+ hydrocarbons

It was noted (Table 3.7) that approximately 25% of the catalyst bed in reactor 4 contained a significant amount of sulfur. However, as seen in Table 3.9, the conversions obtained from the sulfided and unsulfided reactors are very close, i.e. there was no catalyst deactivation. One argument may be that conversion values from the reactors are close because the complete bed does not participate during the reaction, and therefore, even though the sulfided portion of the bed remains inactive, the rest of the catalyst is sufficient to give the appropriate conversion. This argument is valid when conversions of 99-100% are obtained. But, for example, where H_2 conversions of about 30% and CO conversions of about 72% are obtained, the above argument cannot explain the similarity of results on the sulfided and unsulfided catalyst. This is an important result as it shows that a precipitated (ppt) iron-based catalyst, such as the one used here, can withstand deactivation by sulfur to a certain extent.

Let us compare the above results on precipitated iron catalysts to those of Anderson et al. (58) on fused iron catalysts given in Table 3.10. The results indicate that the presence of sulfur causes a significant drop in the catalytic activity of fused iron catalysts as opposed to our results on precipitated iron-based catalysts.

Besides activity, the selectivity values given in parentheses in Table 3.9 are also very uniform and seem to be independent of the presence of sulfur. The selectivity to C_5+ hydrocarbons is quite low, approximately 40%, indicating that about 60% of the CO is utilized to make gaseous hydrocarbons and CO_2.

Table 3.10

USBM Results on a Fused Iron Catalyst (58)

Catalyst 100 Fe : 6.84 MgO : 1.05 SiO_2 : 0.85 K_2O
Particle Size 28-32 Mesh
Temperature = 250 C, P = 2140 kPa, $H_2/CO = 1.0$

Using the data and correlations given by Anderson et al., (58, 59) and assuming that the sulfur free system has H_2 + CO conversion = 90%, we have:

	Total (H_2 + CO) Conversion, %
No Sulfur	90[1]
0.4% S by wt	44

Sulfur Gradient on Catalyst Bed[2]

First 14 cm	95.5%[3]
Next 6 cm	2.7
Final 8 cm	1.8

---

[1] Assumed.

[2] % of total sulfur in bed obtained after approximately 3.3% by wt sulfur had been admitted to the catalyst. It must be noted that at the 0.4 wt % S level the sulfur gradient may be even steeper.

[3] A further breakdown of the sulfur level was not given; it may be reasonable to assume that most of the sulfur is contained at the bed entrance as shown in our experiments (Table 3.7).

The effect of the H_2/CO ratio is given in Table 3.11. There is a slight increase in contraction and overall conversion as the H_2/CO ratio is reduced. More CO_2 and less gaseous hydrocarbons are produced when $H_2/CO = 1$. The amount of CO converted to C_5+ is independent of the reactant ratio. The olefinic content of the gaseous hydrocarbons are substantially increased when $H_2/CO = 1$. The only effect of sulfur can be seen for $H_2/CO = 1.6$ when the gaseous products from reactor 4 are consistently more olefinic than the products from the unsulfided catalyst. Except for ethylene production, this is not the case when $H_2/CO = 1$. The effect of the H_2/CO ratio is more substantial than the effect of sulfur.

The effect of space velocity is given in Table 3.12. Gas contraction and overall conversion are slightly enhanced by decreasing the space velocity. The effect of space velocity on product selectivity is minimal. However, a high space velocity does favor the production of gaseous olefins. At the higher space velocity substantially larger amounts of ethylene are formed in reactor 4 than in reactor 5; however, a similar sulfur effect is not seen for propylene and butene formation. The effect of sulfur for olefin production is negligible at the low space velocity.

Some results of the effect of temperature are given in Table 3.13 and Figure 3.6 and 3.7. There is a rapid increase in methane production between 505 and 525 K. With further increase in temperature, there is a slight initial increase in methane formation, and then a decrease is noted after 535 K (Figure 3.5). In the case of CO_2 formation, there is a rapid decrease between 505 and 525 K. However, as shown by the horizontal dashed line in Figure 3.6, the % conversion of CO to C_5+ hydrocarbons is independent of temperature. These trends in selectivity are the same for both sulfided and unsulfided catalysts. As shown in Figure 3.7 the amount of CO consumed to give gaseous hydrocarbons increases with temperature. At 500 K more ethylene is produced than ethane, but as soon as the temperature is raised to 513 K the trend is reversed. The effect of temperature on propylene and 1-butene formation is not as drastic as with ethylene formation, and in all cases more propylene and 1-butene are formed than the corresponding alkanes.

The effect of pressure on CO_2 formation and C_5+ hydrocarbon formation is small (Table 3.14). The effect of pressure on CH_4 formation is shown in Figure 3.8, and a sulfur effect can also be perceived. At low pressures there is no effect of sulfur, but after 15 MPa the CH_4 produced by the unsulfided catalyst and the catalyst containing 0.08% S by wt % becomes independent of pressure. The CH_4 produced by the more highly sulfided catalyst, however, continues to increase with pressure. At low pressures (Table 3.14, Figure 3.7) the ratio, CO converted to C_5+/CO converted to hydrocarbon gas, is larger than 5. As the pressure is increased to 25 MPa this ratio falls rapidly to about 2.25. This indicates that at the lower pressure more CO is converted to condensed hydrocarbons rather than to gaseous hydrocarbons. Table 3.15 and Figure 3.9 show the effect of pressure on olefin production. Low pressures favor the production of more ethylene than ethane, but as the pressure is raised from 5 to 10 MPa this trend is reversed. This pressure effect is similar to the one described above for temperature. A slight sulfur effect can be seen with respect to the ethylene/ethane ratio at low pressures; at higher pressures, this sulfur effect becomes negligible (Figure 3.9). The ratios of propylene/propane and 1-butene/n-butane also decrease as the pressure is increased. There is no sulfur effect in these cases, and the amount of C_3H_6 and C_4H_8 produced is always greater than the corresponding paraffin.

Table 3.11

Effect of H_2/CO Ratio
Precipitated Iron-based Catalyst

T = 523 K ± 0.05%, P = 1010 kPa ± 4%, SV = 195 V/V/h ± 9%

H_2/CO	1.61				1.03			
Reactors	1	3	4	5	1	3	4	5
Nominal Sulfur, wt %	0.08	0.24	0.40	0	0.08	0.24	0.40	0
CO_2-free contraction, %	74.1	76.2	75.8	76.6	84.3	84.2	85.4	84.4
H_2 + CO converted, %	78.5	81.8	80.0	81.3	87.4	87.1	88.1	87.2
Selectivity[1], % CO converted to:								
CO_2	36.7	33.7	35.2	32.0	45.8	39.3	40.9	44.4
CH_4	7.1	6.9	6.2	6.7	4.7	5.1	4.7	4.5
C_5+	31.7	37.7	39.4	39.5	35.4	43.9	43.0	38.3
CO to C_5+/CO to hydc. gas	1.00	1.31	1.55	1.40	1.88	2.62	2.69	2.20
Olefins:								
Ethylene/Ethane	0.14	0.16	0.19	0.12	0.33	0.25	0.35	0.27
Propylene/Propane	3.11	2.83	3.23	2.69	4.89	3.84	4.33	4.62
1-Butene/n-Butane	2.39	2.17	2.50	2.05	4.16	3.16	3.58	3.80

---

[1] Selectivity is based on the total amount of CO converted.

Table 3.12

Effect of Space Velocity
Precipitated Iron-based Catalyst

T = 512 K ± 0.01%, P = 1010 kPa ± 4%, H_2/CO = 1.51 ± 3%

Space Velocity, V/V/h	109				250			
Reactors	1	3	4	5	1	3	4	5
Nominal Sulfur, wt %	0.08	0.24	0.40	0	0.08	0.24	0.40	0
CO_2-free contraction, %	69.5	68.2	71.6	68.8	66.3	65.4	65.1	64.5
H_2 + CO converted, %	71.1	70.7	74.0	70.4	66.7	65.7	65.7	65.5
Selectivity, % CO converted to:								
CO_2	42.1	41.6	40.5	45.7	49.1	46.3	46.9	48.2
CH_4	3.3	3.8	3.9	3.4	2.9	3.0	3.0	2.8
C_5+	42.8	41.9	42.6	38.2	37.4	40.0	39.1	38.8
CO to C_5+/CO to hydc. gas	2.84	2.52	2.51	2.35	2.77	2.92	2.81	2.98
Olefins:								
Ethylene/Ethane	0.11	0.10	0.10	0.09	0.56	0.55	0.81	0.49
Propylene/Propane	2.59	2.58	2.68	2.70	4.72	4.09	4.48	4.33
1-Butene/n-Butane	2.07	2.15	2.17	1.85	3.81	3.22	3.56	3.57

Table 3.13

Effect of Temperature
Precipitated Iron-based Catalyst

P = 1010 kPa ± 4%, SV = 250 V/V/h ± 6%, H_2/CO = 1.51 ± 3%

Temperature[1]	500 K				513 K				522 K			
Reactors	1	3	4	5	1	3	4	5	1	3	4	5
Nominal Sulfur, wt %	0.08	0.24	0.40	0	0.08	0.24	0.40	0	0.08	0.24	0.40	0
Selectivity, % CO converted to:												
CO_2	44.9	45.6	47.7	49.3	49.2	46.3	46.9	48.2	41.5	34.6	34.7	37.3
CH_4	2.1	2.3	2.5	2.1	2.9	2.9	3.0	2.8	7.4	6.2	6.3	6.5
C_5+	43.9	42.3	39.5	39.9	37.4	40.0	39.1	38.8	29.0	43.2	43.1	36.2
CO to C_5+/CO to hydc. gas	3.90	3.49	3.06	3.71	2.77	2.92	2.81	2.98	0.98	1.94	1.94	1.36
Olefins:												
Ethylene/Ethane	1.37	1.45	1.74	1.54	0.56	0.55	0.81	0.50	0.23	0.20	0.23	0.16
Propylene/Propane	4.40	4.19	4.14	4.28	4.73	4.09	4.48	4.33	3.81	3.36	3.51	3.47
1-Butene/n-Butane	3.51	3.22	3.32	3.40	3.81	3.20	3.56	3.58	2.87	2.85	2.82	2.79

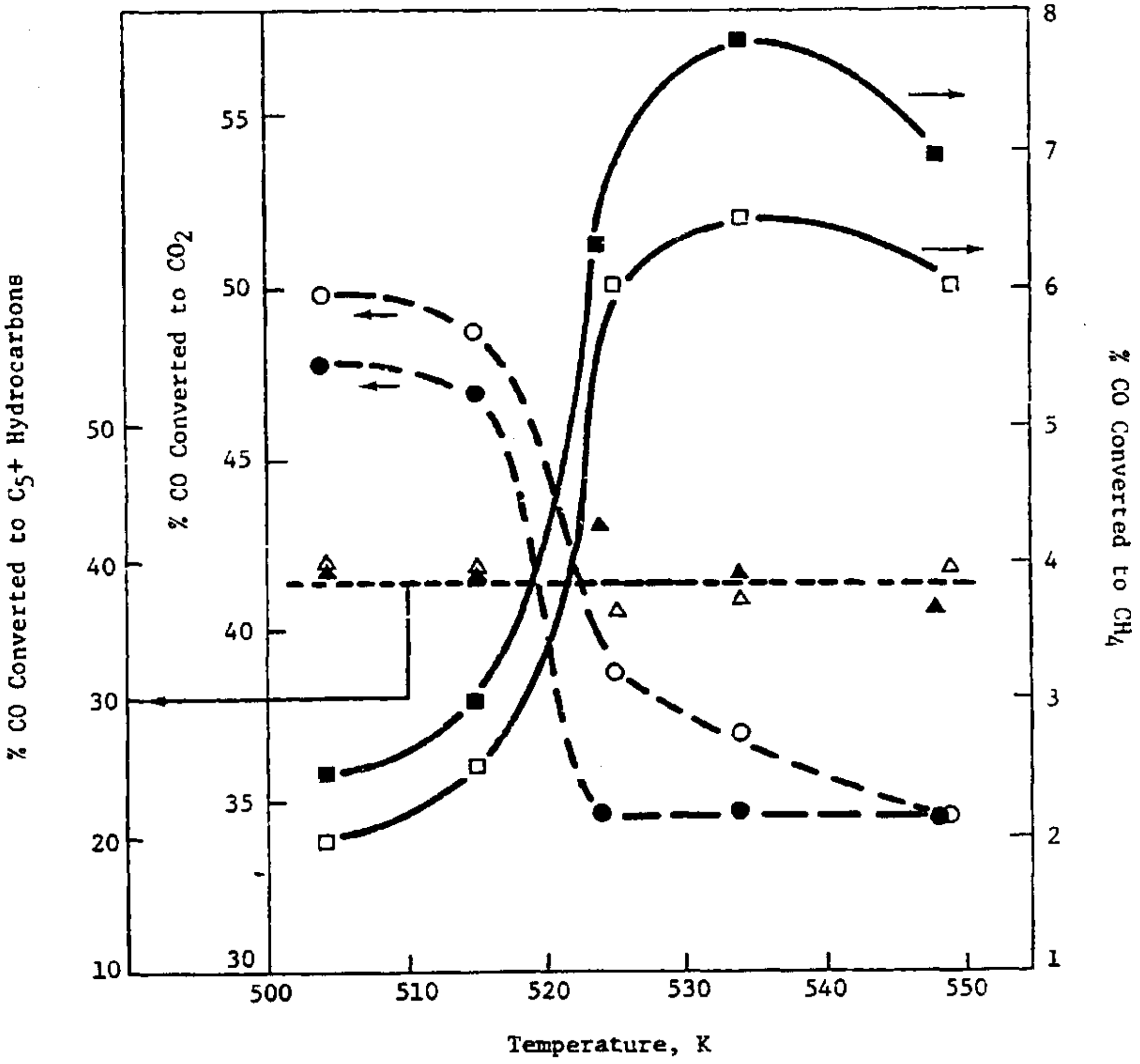
---

[1] Error < 0.1%

Figure 3.6

Selectivity versus Temperature
Precipitated Iron-based Catalyst

P = 1010 kPa, SV = 250 V/V/h, H_2/CO = 1.51

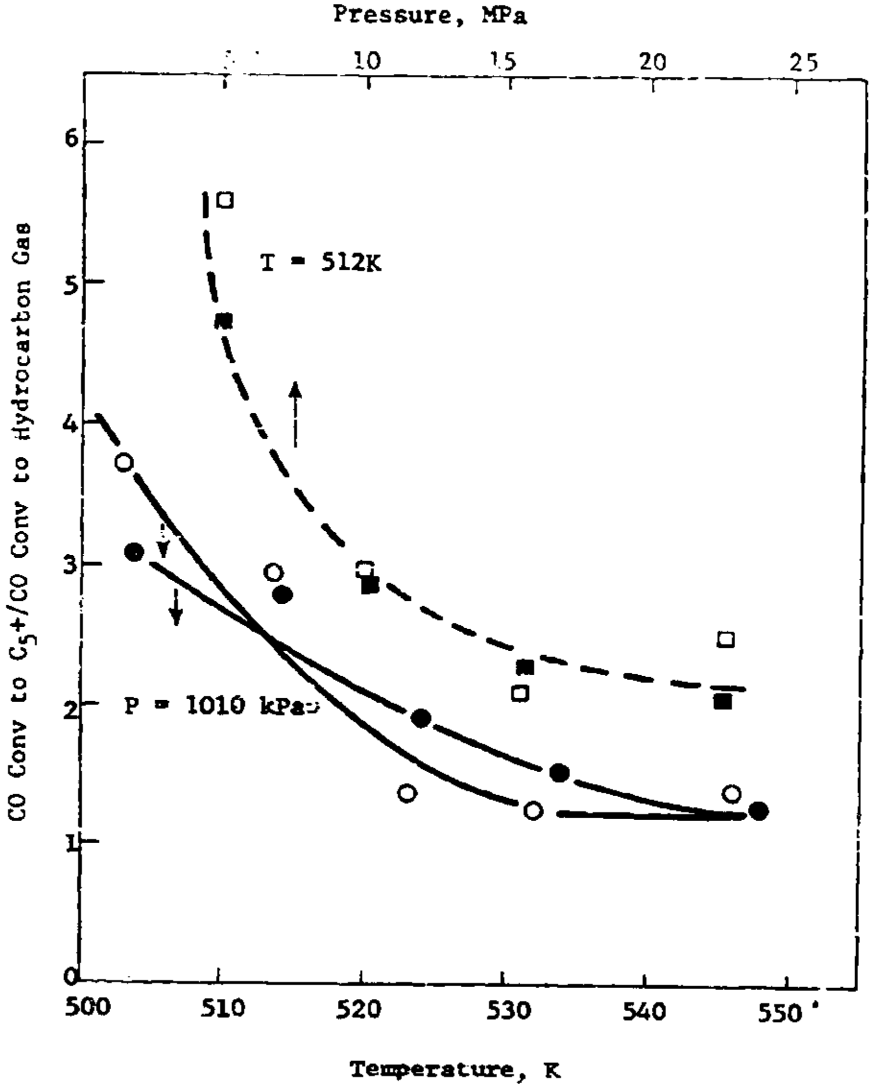


Hollow points correspond to the unsulfided catalyst.
Solid points correspond to the catalyst with 0.4 wt % sulfur.

Figure 3.7

The Effect of Temperature and Pressure on the Formation of Gaseous and Condensed Hydrocarbons Precipitated Iron-based Catalyst

SV = 250 V/V/h, H_2/CO = 1.5



Hollow points correspond to the unsulfided catalyst.
Solid points correspond to the catalyst with 0.4 wt % sulfur.

Table 3.14

Effect of Pressure on Selectivity Precipitated Iron-based Catalyst

T = 512 K ± 0.05%, SV = 250 V/V/h ± 5%, H_2/CO = 1.49 ± 2%

	% CO Conv. to CO_2				% CO Conv. to CH_4				% CO Conv. to C_5+				CO to C_5+/CO to hydc. gas			
Reactors	1	3	4	5	1	3	4	5	1	3	4	5	1	3	4	5
Nominal Sulfur, wt %	0.08	0.24	0.40	--	0.08	0.24	0.40	1.5	0.08	0.24	0.40	--	0.08	0.24	0.40	--
Pressure, kPa																
500	58.9	47.5	53.1	54.5	1.52	1.60	1.71	1.5	54.1	45.0	38.7	38.7	4.84	6.02	4.71	5.62
1010	49.2	46.3	47.0	48.2	2.91	2.98	2.99	2.75	37.4	40.0	39.1	38.8	2.77	2.92	2.81	2.98
1550	47.2	53.6	48.7	49.9	3.46	3.89	3.35	3.27	36.8	28.3	35.6	34.0	2.30	1.55	2.26	2.11
2290	38.8	43.5	42.4	40.7	3.30	4.64	4.17	3.28	45.4	36.1	38.7	42.8	2.88	1.77	2.06	2.57

Figure 3.8

Effect of Sulfur and Pressure on CH_4 Formation
Precipitated Iron-based Catalyst

T = 512 K, SV = 250 V/V/h, H_2/CO = 1.49

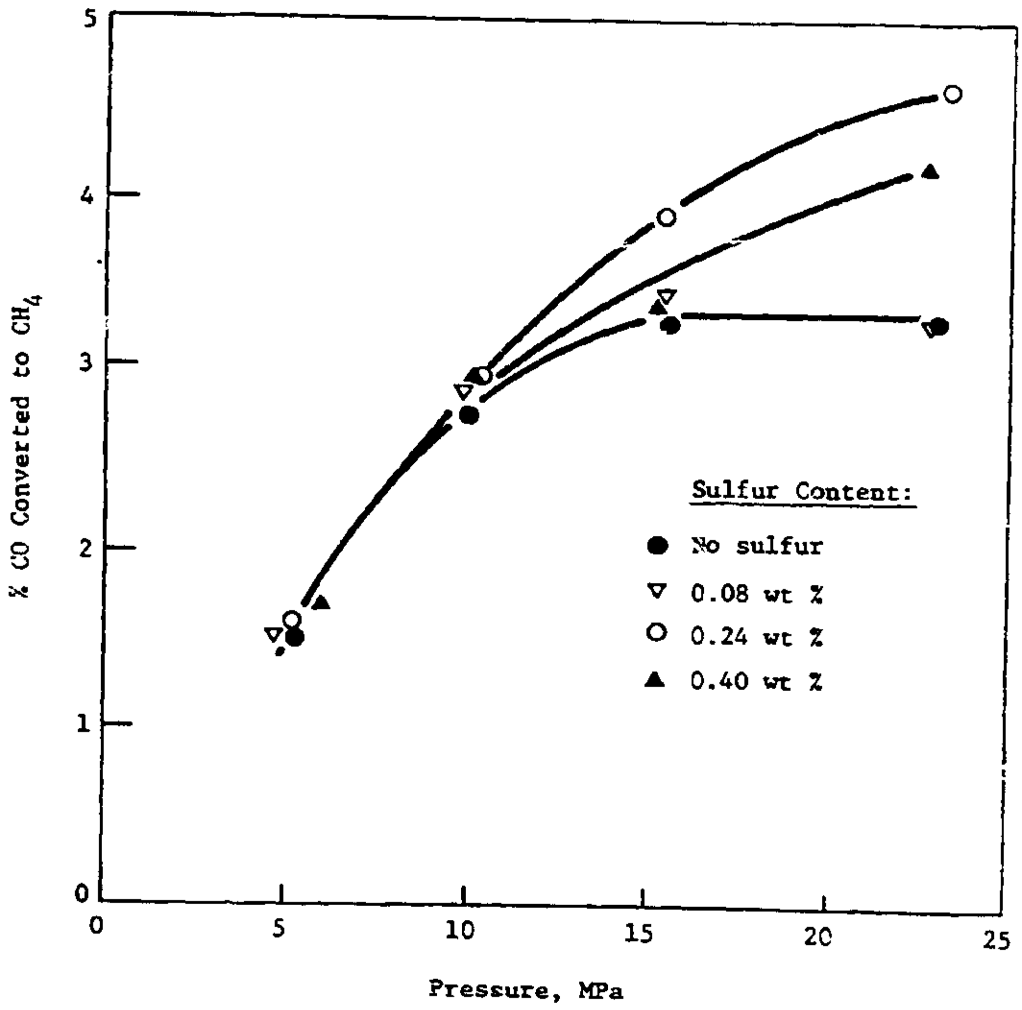


Table 3.15

Effect of Pressure on Olefins in Gaseous Products Precipitated Iron-based Catalysts

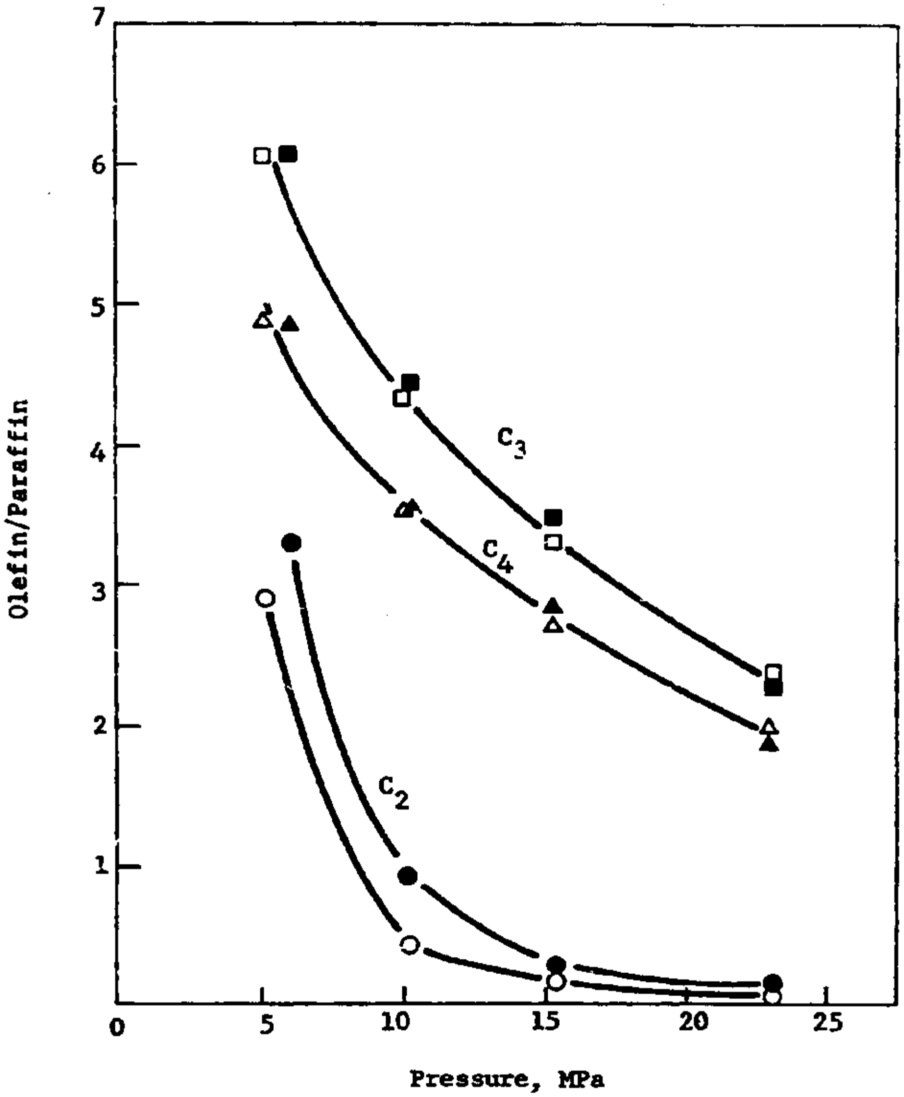
T = 512 K ± 0.05%, SV = 250 V/V/h ± 5%, H_2/CO = 1.49 ± 2%

	Ethylene/Ethane				Propylene/Propane				1-Butene/n-Butane			
Reactors	1	3	4	5	1	3	4	5	1	3	4	5
Nominal sulfur, wt %	0.08	0.24	0.40	--	0.08	0.24	0.40	--	0.08	0.24	0.40	--
Pressure, kPa												
500	3.03	2.64	3.29	2.93	5.93	6.19	6.05	6.07	4.65	4.42	4.83	4.90
1010	0.56	0.55	0.81	0.49	4.73	4.09	4.48	4.34	3.81	3.19	3.56	3.58
1550	0.12	0.20	0.26	0.15	3.09	3.28	3.47	3.29	2.55	2.64	2.85	2.70
2290	0.03	0.04	0.10	0.07	2.15	2.10	2.30	2.35	1.80	1.76	1.91	1.97

Figure 3.9

Effect of Pressure on the Olefin/Paraffin Ratic of Gaseous Hydrocarbons
Precipitated Iron-based Catalyst

T = 512 K, SV = 250 V/V/h, H_2/CO = 1.49



Hollow points correspond to the unsulfided catalyst.
Solid points correspond to the catalyst with 0.4 wt % sulfur.

The distribution of condensed products for several experiments is listed in Appendix E. Figures 3.10, 3.11 and 3.12 show distribution of products as carbon number, which includes mainly n-paraffins and α-olefins. In all three cases, which represent experiments at different pressures, there is an initial sharp rise with a maximum at C_{11}-C_{12} and then a gradual decline to C_{45}. Small amounts of products between C_{45} and C_{55} were seen on the chromatograph trace but were too small to be picked up by the computer. Unlike the results from cobalt, there is little observable sulfur or pressure effect here, and there is no evidence of any bi-modal distribution of products.

Table 3.16 compares the results obtained with cobalt and iron catalysts, at similar conditions and CO_2-free contractions. The reaction temperature, however, is 55°C lower for the more active cobalt catalyst. The most important result is that the selectivity for CO conversion to C_5+ hydrocarbon is twice as high on cobalt than on iron. Correspondingly, iron catalysts produce more gaseous hydrocarbons and 10 times more CO_2. It is important to note the larger amount of the water-gas shift reaction taking place on iron. This may be due to the higher temperatures which have to be used with the less active iron catalysts. Hence, besides being more active, the cobalt catalyst is much more efficient for producing condensed hydrocarbons. The iron catalyst forms more ethylene, propylene and 1-butene than cobalt on which the formation of ethylene is negligibly small.

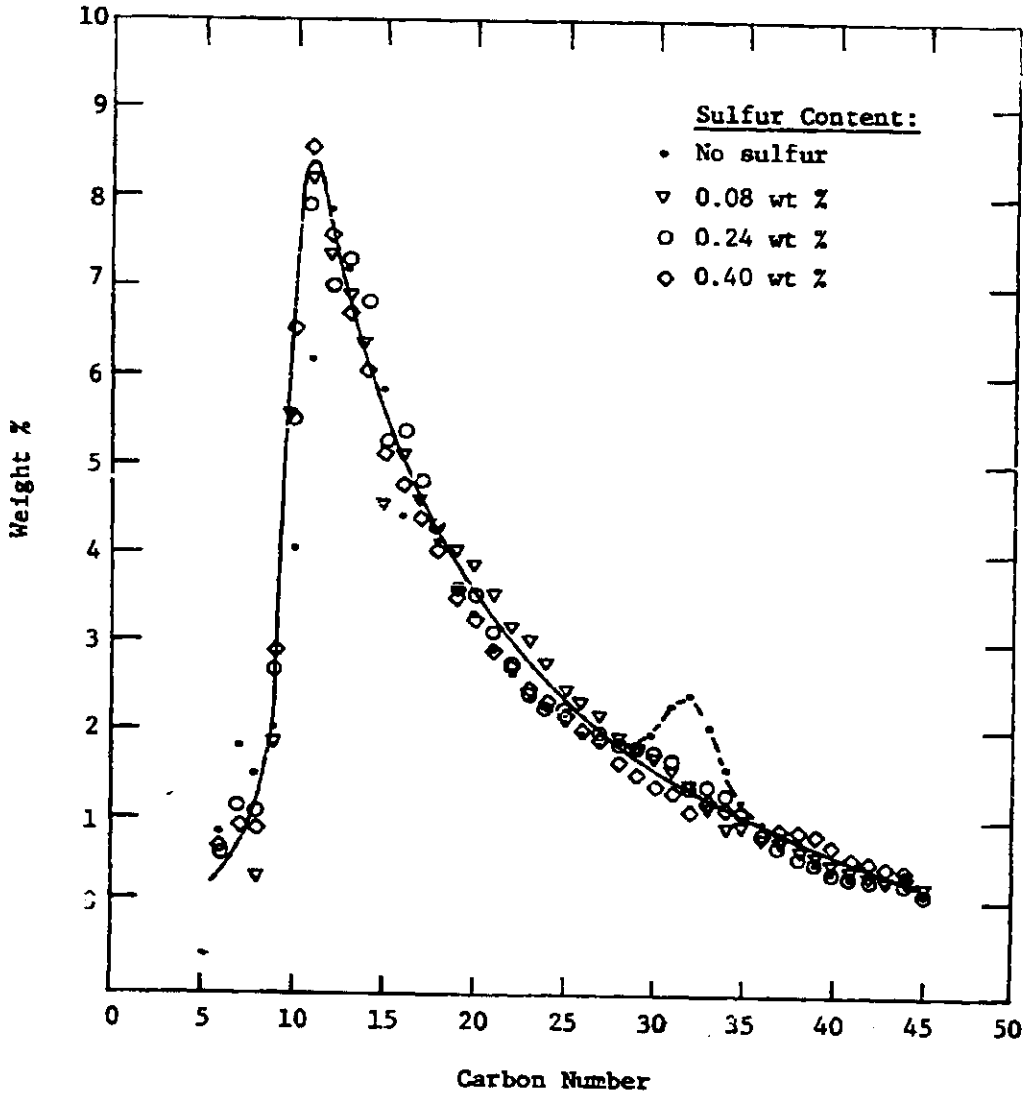
Our results may be compared to those of Rapoport and Muzovskaya who showed (60, 61 , 62) that precipitated Fe-Cu catalysts, reduced in H_2 under mild conditions (200°C), worked without deactivation in synthesis gas containing 50 to 100 ppm COS and CS_2 for long periods of time. They noted that the presence of FeO was essential for resistivity to deactivation by sulfur. They further noted that if the catalyst was reduced in H_2 at temperatures greater than 400°C the iron was in the metallic form, and the catalyst was easily poisoned by sulfur. These interesting results of Rapoport and Muzovskaya, which have been discussed in detail elsewhere (6), together with our results on precipitated Fe-based catalysts, which were also reduced under mild conditions ($H_2/CO = 1$, $T = 240°C$), show that it may be possible to formulate sulfur resistant FT iron-based catalysts. At present, it is difficult to say what surface state of iron is the active state, and whether metallic iron is required. However, precipitated Fe-based catalysts, reduced under mild conditions, act differently from the popular fused iron catalysts which as shown in Table 3.10 deactivate rapidly in the presence of sulfur.

X-ray diffraction measurements of our raw unused catalyst indicated that only α-Fe_2O_3 was present; measurements at the end of the FT synthesis run indicated that only Fe_3O_4 was present. It is probable that small amounts of metallic surface iron, carbides or other compounds were oxidized when the catalyst was removed from the reactor.

Figure 3.10

Distribution of Condensed Products
Precipitated Iron-based Catalyst

P = 1000 kPa, SV = 250 V/V.h, T = 240°C, H_2/CO = 1.46



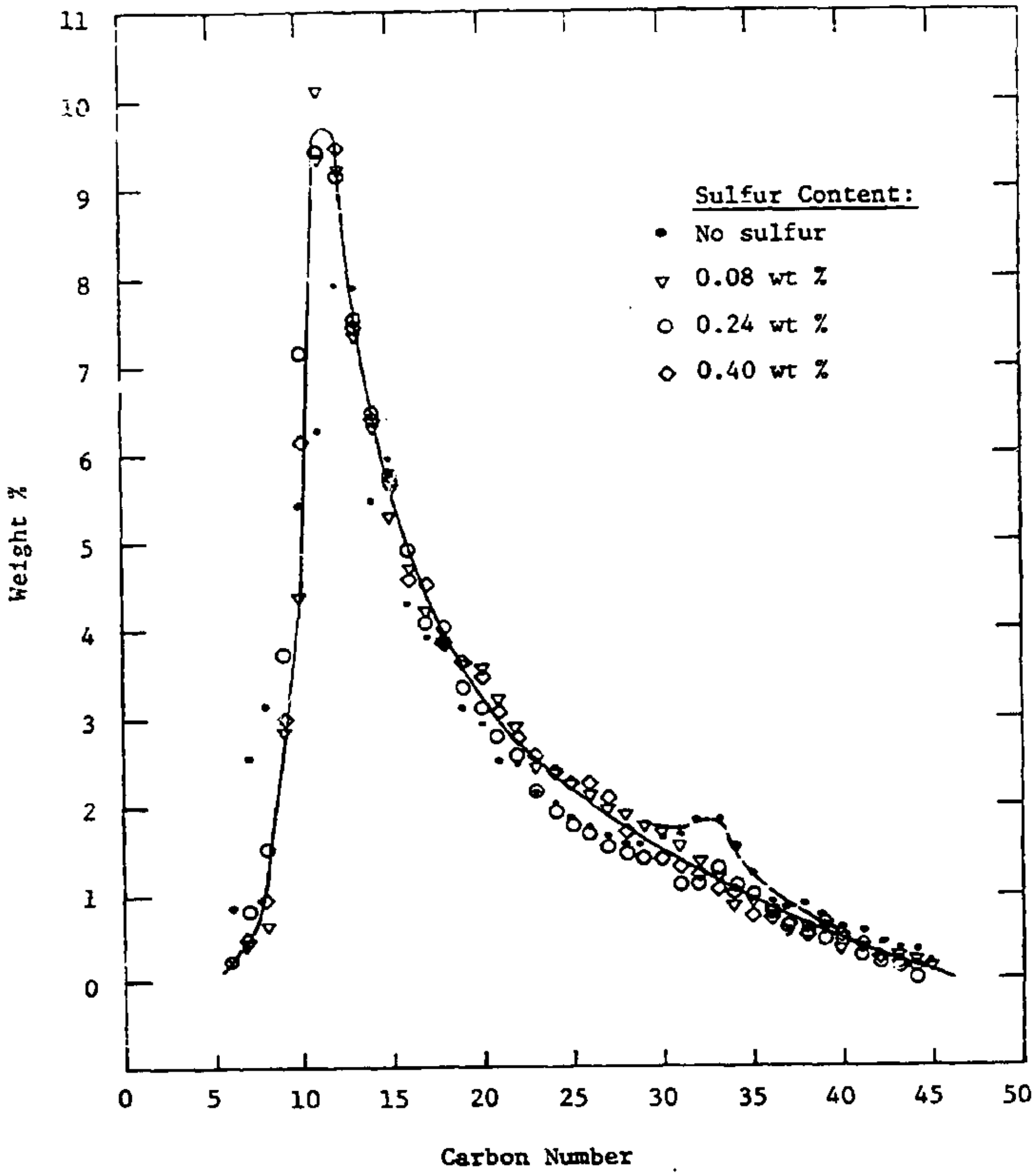


Figure 3.11

Distribution of Condensed Products
Precipitated Iron-based Catalyst

P = 1550 kPa, SV = 250 V/V/h, T = 240°C, H_2/CO = 1.49

Figure 3.12

Distribution of Condensed Products
Precipitated Iron-based Catalyst

P = 2300 kPa, SV = 250 V/V/h, T = 240°C, H_2/CO = 1.51

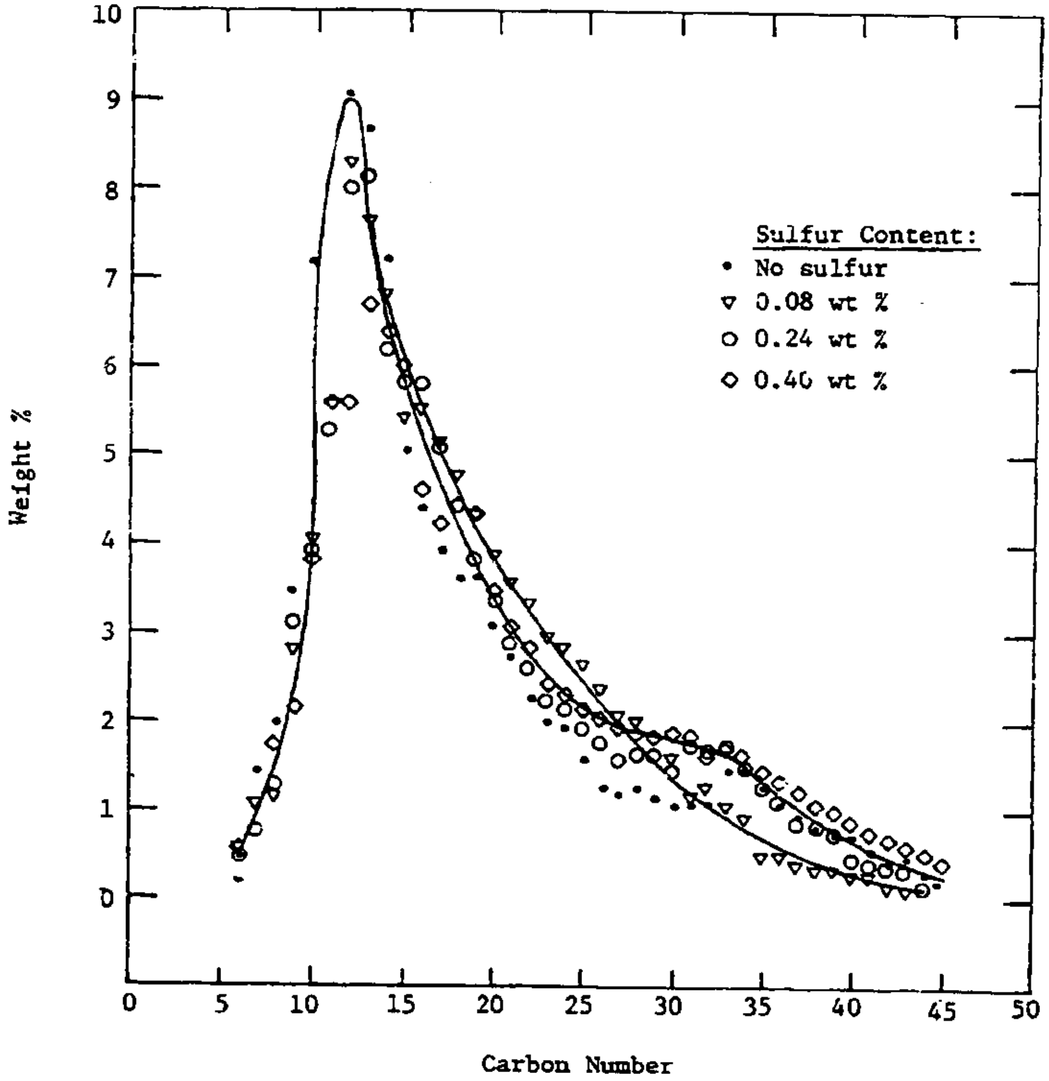


Table 3.16

Comparison of Precipitated Cobalt-based and Iron-based Catalysts

Co : ThO_2 : kieselguhr : K_2CO_3 (Unsulfided); SV = 208 V/V/h, P = 1100 kPa, $H_2/CO = 1.53$

Fe : Cu : K_2CO_3 (Unsulfided); SV = 196 V/V/h, P = 1000 kPa, $H_2/CO = 1.61$

	Ppt Co-based	Ppt Fe-based
Reaction temperature, °C	195	250
CO_2-free contraction, %	79.1	76.6
H_2 conversion, %	90.0	70.7
CO conversion, %	67.1	99.3
CO converted to hydrocarbons, %	65.1	66.3
H_2 usage ratio	0.67	0.53
Selectivity, % CO converted to:		
CO_2	2.9	32.6
CH_4	4.7	6.7
$C_2H_4 + C_2H_6$	1.8	6.9
$C_3 + C_4$	10.4	14.3
C_5+	80.2	39.5
CO conv. to C_5+/CO conv. to gas[1]	3.71	0.65
Gaseous olefin production		
C_2H_4/C_2H_6	~ 0	0.12
C_2H_4/C_3H_8	2.23	2.69
$1\text{-}C_4H_8/n\text{-}C_4H_{10}$	1.36	2.05

---

[1] CH_4 to C_4 hydrocarbons + CO_2

3.2.4 Summary

- It was shown that the primary reaction forms hydrocarbon and water, whereas the CO_2 is produced by the water-gas shift reaction.

- The addition of sulfur did not deactivate the precipitated iron-based catalyst. This result was compared to similar observations made in the past by Rapoport and Muzovskaya (60, 61, 62).

- On comparing our work and the work of Rapoport and Muzovskaya on precipitated iron-based catalysts with the work on fused iron catalyst by Anderson et al. (58), it was seen that the fused iron catalysts deactivate much more rapidly in the presence of sulfur.

- There was no significant sulfur effect except in the production of ethylene. The catalyst containing 0.4 wt % S consistently produced more ethylene than the unsulfided catalyst.

- More ethylene than ethane was produced only at the lowest temperature (500 K) and pressure (5 MPa) studied. However, more propylene and 1-butene were produced than the corresponding alkanes at all conditions studied.

- The ratio, CO converted to C_5+ hydrocarbons/CO converted to hydrocarbon gas, was higher at low temperatures and low pressures.

- Depending on the experimental conditions, approximately 30 to 40% of the CO reacted was converted to C_5+ hydrocarbons, and approximately 35 to 50% of the CO reacted was converted to CO_2. There was no marked effect of sulfur on these selectivities. The highest selectivity to form CO_2 was obtained at the lowest temperature and pressure used.

- The condensed product distribution did not show a strong dependence on pressure or on the amount of sulfur present on the catalyst. A skew distribution was obtained, and a single maximum at C_{11}-C_{13} was seen in all cases.

3.3 Cobalt-Molybdenum Catalysts

3.3.1 Catalyst Pre-treatment and Sulfiding

The catalyst used was a commercial hydrotreating catalyst, made by Harshaw Chemical Company, containing nominally 3% cobalt oxide and 11% molybdenum trioxide supported on alumina. The catalyst is sold under the commercial name HT-400. This catalyst was used (a) without any promoter, and (b) after being impregnated with K_2CO_3 so that the alkali content, calculated as K_2O, was 3.45% by weight of the total catalyst.

The reactors, after being loaded with the catalysts as shown in Table 3.17, were assembled on the unit and flushed and pressure tested with He. The catalysts were then dried overnight (approximately 15 h) under a flow of He at 150°C. Reactors 2 and 4 were shut off and held under a He pressure of 500 kPa. Catalysts in reactors 1, 3, 5, 6, and 7 were treated in H_2, 600 V/V/h, at atmospheric pressure as follows: the temperature was increased in 50°C increments up to 450°C, and the catalysts were reduced at 450°C for 24 h. The reactors were then flushed with He. Catalysts in reactors 1 and 3 were sulfided with 0.103% H_2S in H_2, at 300°C, atmospheric pressure and a space velocity of 500 V/V/h, to obtain a nominal sulfur content of 1% by wt. The reactors were once again flushed with He.

All reactors, except 2 and 4, were shut off and kept under He at 500 kPa. Catalysts in reactors 2 and 4 were first calcined in air, 480 V/V/h, at 400°C for 2 h. The temperature was reduced to 42°C, and the reactors were flushed with He. A flow of 10% H_2S in H_2, 700 V/V/h, was started; within 8 min the temperature increased from 42°C to 48°C and decreased again to 42°C as the exotherm passed through the bed. The temperature was kept at 42°C for 1 h, then raised to 150°C for 1 h and finally increased to 320°C. Sulfiding was continued with the 10% H_2S/H_2 mixture at 320°C for 15 h, after which the reactors were flushed with He. Catalysts in reactors 2 and 4 will be called fully sulfided catalysts. The sulfiding proceeding was recommended by Harshaw. All pretreatment procedures were carried out at atmospheric pressure.

Table 3.17 summarizes the catalysts and the individual pretreatment procedures.

Table 3.17

Summary of Catalysts in Run 6

Symbol	Reactor	Catalyst[1]	Pretreatment
CM-R	5	HT-400	Reduced in H_2
CM-RS	1	HT-400	Reduced in H_2 and then sulfided nominally 1% by wt S
CM-S	2	HT-400	Calcined and fully sulfided
CMK-R	6 and 7	HT-400 + K_2O	Reduced in H_2
CMK-RS	3	HT-400 + K_2O	Reduced in H_2 and then sulfided nominally 1% by wt S
CMK-S	4	HT-400 + K_2O	Calcined and fully sulfided

---

[1] 50 cm^3 of 60-120 mesh particles were used in each reactor. The weight of catalyst HT-400 loaded into each reactor was 34.25 g, whereas the weight of catalyst HT-400+K_2O in each reactor was 36.10 g.

At the end of the run a detailed longitudinal sulfur gradient analysis was done (Table 3.18). The catalyst to be analyzed was removed from the reactor in equal sections. Each section corresponded approximately to 5 cm of reactor length. In Table 3.18, section 1 corresponds to the first 5 cm of the inlet side of the reactor, section 2 corresponds to the next 5 cm of reactor length, etc. The sulfur analysis was based on the weight of the catalyst.

Table 3.18

Longitudinal Sulfur Distribution in Catalyst Beds for Run 6

Catalyst	CM-RS	CM-S	CMK-RS	CMK-S
Section	Reactor 1 % S by wt	Reactor 2 % S by wt	Reactor 3 % S by wt	Reactor 4 % S by wt
1	1.65	4.71	1.99	4.61
2	1.88	4.79	1.84	5.05
3	1.83	4.95	1.76	5.05
4	1.85	5.18	1.55	5.04
5	1.62	5.13	1.52	4.98
6	1.49	5.03	1.37	5.02
7	1.61	4.96	1.36	4.90
8	1.22	4.80	1.31	4.87
9	1.45	5.00	1.24	5.05
10	1.41	4.89	1.06	5.05
11	1.23	4.76	1.03	4.81
12	1.16	5.24	0.80	5.10
13	0.74	5.26	0.25	4.98
14	0.17	5.31	0.03	4.99
15	< 0.01	5.06	0.01	5.17
16	< 0.01	4.90	< 0.01	4.93
17	< 0.01	5.14	0.02	5.02
18	< 0.01	5.07	< 0.01	4.98

Approximately 70% of the catalyst beds in reactors 1 and 3 contain most of the sulfur, and the sulfur distribution is fairly even. It is interesting to note that the sulfur gradient in the catalyst containing alkali (reactor 3) is continuous and slightly steeper than the identically treated, non-alkalized catalyst in reactor 1. In reactors 2 and 4 where the complete sulfidation of the catalyst was attempted, the sulfur distribution is even and very similar in both reactors. The sulfur content in reactors 5, 6, and 7 was negligibly small throughout the bed, the nominal sulfur content being < 0.02% S by wt.