3. CATALYST EVALUATION

3.1 Precipitated Cobalt-based Catalyst

3.1.1 Catalyst Pre-treatment and Sulfiding

Seven reactors were filled with 50 cm^3 (29.8 g) of 60 to 120 mesh 100 Co : 15.9 ThO_2 : 92.9 kieselguhr : 1.96 K_2CO_3 catalyst. The reactors, after being assembled on the unit, were first flushed and then pressure tested with He. The pressure (P) was then reduced to atmospheric pressure, and the temperature (T) of the catalyst was then raised to 400°C (752°F) under flowing H_2 at a space velocity (SV) of 350-375 V/V/h. The catalyst was then reduced for 4 h in flowing H_2 at atmospheric pressure and 400°C. The catalyst temperature was dropped to 140°C in flowing H_2. The catalysts in all the reactors were then treated at atmospheric pressure with flowing H_2 and CO (H_2/CO = 2) at a space velocity of 300 V/V/h: first at 140°C for 1 h, at 150°C for 1 h, at 165°C for 13 h, at 170°C for 8 h and finally at 180°C for 18 h. The reactors were finally flushed with He before sulfiding.

Reactors 5, 6 and 7 were isolated from the gas manifold and kept under He while reactors 1, 2, 3 and 4 were being sulfided at 180°C and atmospheric pressure. A 2:1 mixture of H_2:CO containing 250 ppm H_2S was used at a space velocity of approximately 300 V/V/h. No H_2S was detected coming out of the reactors during the sulfiding process. Table 3.1 gives the nominal sulfur levels calculated as weight % of unreduced catalyst and as mg S per g of Co.

Table 3.1

Nominal Sulfur Levels on Cobalt-based Catalyst Used in Run 4

Reactor	Nominal Sulfur Level as wt % of unreduced catalyst	 as mg S/g Co
1	0.29	8.2
2	0.43	12.2
3	0.50	14.2
4	0.50	14.2
5	—	—
6	—	—
7	—	—

As nominal sulfur levels do not give complete information regarding the amount of sulfur on the catalyst, a detailed longitudinal sulfur gradient analysis was done (Table 3.2). At the end of run 4 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 3.2 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 after all carbon had been removed, i.e. the wt % reported is not masked by the wax on the spent catalyst.

Table 3.2

Longitudinal Sulfur Distribution in Catalyst Beds for Run 4

Section	Reactor 1 % S by wt	Reactor 2 % S by wt	Reactor 3 % S by wt	Reactor 4 % S by wt
1	4.96	5.36	7.66	7.57
2	1.32	2.07	2.53	2.17
3	1.02	0.81	1.38	0.74
4	0.06	0.09	0.05	0.05
5	0.05	0.04	0.08	0.06
6	0.03	0.46	0.01	0.02
7	0.03	0.16	0.04	0.05
8	0.01	0.13	0.02	0.03
9	0.02	0.08	0.04	0.03
10	0.03	0.07	0.04	0.05
11	0.01	0.10	0.05	0.01
12	0.02	0.09	0.02	0.02
13	0.01	0.08	0.02	0.05
14	0.01	0.10	0.03	0.03
15	0.01	0.03	0.02	0.01
16	0.01	0.08	0.01	0.02
17	0.01	0.04	0.02	0.06

In all cases the inlet portion (first 20%) of the bed contains most of the sulfur. The amount of sulfur after the first 20% of bed length is greater in reactor 2 than in the other reactors, i.e. sulfur distribution is a little better in reactor 2, therefore it will be especially important to compare the results obtained from reactor 2 with other results in the run. Sulfur in reactors 5, 6, and 7 was negligibly small throughout the bed, nominal sulfur content being < 0.01 % S by weight.

3.1.2 Experiments Performed

Before discussing the complete run, let us list the experiments in the order that they were performed (Table 3.3). After each experiment the catalyst was kept overnight in flowing H_2 at the same temperature and pressure used in the experiment. The flow of H_2 was stopped just before the next experiment was started. This catalyst conditioning has been recommended for Co catalysts (38), and it was used by us in order to prevent the catalyst from undergoing drastic changes during the course of the run. The following table gives the experimental conditions and duration of each test:

Table 3.3

Experimental Conditions[1] for Run 4

Experiment	H_2/CO	SV, V/V/h	T, °C	P, kPa	Time, h
4-1	1.85	217	195	600	3.3
4-2	1.49	204	195	600	4.2
4-3	2.06	248	197	600	5.4
4-4[2]	1.94	210	197	1100	3.9
4-5	1.53	200	195	1100	4.8
4-6	2.01	210	197	1100	4.7
4-7	1.97	209	197	1600	3.8
4-8	2.02	210	215	1600	4.0

3.1.3 Results and Discussion

Let us first compare the activity and selectivity to C_5+ hydrocarbons for the several experiments (Table 3.4). The activity may be stated as a percent conversion of H_2 and CO.

Table 3.4

Conversion of H_2 and CO on Cobalt-based Catalyst

T = 197 ± 3°C

	Total Hydrogen Converted, %				Total Carbon Monoxide Converted, %			
Reactor	1	2	4	5	1	2	4	5
Nominal S, wt %	0.29	0.43	0.50	0	0.29	0.43	0.50	0
Experiment								
4-1	87	77	74	92	83(81)	73(85)	71(85)	90(84)
4-2	89	80	86	88	70(83)	59(81)	67(85)	67(83)
4-3	92	87	91	88	89(82)	84(74)	88(74)	85(82)
4-4	98	95	98	97	97(79)	87(80)	99(75)	96(78)
4-5	91	86	88	90	70(82)	68(86)	65(78)	67(80)
4-7	96	68	89	88	98(84)	61(71)	84(83)	85(75)

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

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[1] Accurate experimental conditions for each reactor and detailed results are given in the tables for run 4 in Appendix D, pages 136 to 143.

[2] Experiment 4-4 was performed after the catalyst had been in flowing H_2 for about 65 h.

The conversions during all the experiments were high. The lowest conversion of CO, Experiment 4-2 and 4-5, was at conditions where the H_2/CO ratio was 1.5 rather than 2. The hydrogen conversion, however, was not affected by this ratio. It is important to compare H_2 and CO conversions on sulfided and unsulfided catalysts. In Experiment 4-1 results from reactors 2 and 4, and in Experiment 4-7 results from reactor 2 gave conversions 20 to 30% below those obtained from the unsulfided catalyst. This is a reasonable observation as about 20% of the catalyst bed has a significant amount of sulfur. However, under certain other experimental conditions, Experiments 4-2 to 4-5, the conversions obtained from all reactors were close; no significant deactivation was observed. One argument may be that conversion values from all 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, in Experiment 4-5 where H_2 conversions of about 90% and CO conversions of about 70% 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 under certain conditions a cobalt-based catalyst, such as the one used here, can withstand deactivation by sulfur to a certain extent.

The selectivity values given in parentheses in Table 3.4 are very uniform and seem to be independent of the presence of sulfur and the reaction conditions used by us. The selectivity to C_5+ hydrocarbons is also quite high, approximately 75 to 85%, indicating that less than 25% of the CO is used to make gaseous hydrocarbons and CO_2.

The olefin content of gaseous products is given in Table 3.5.

Table 3.5

Olefins in Gaseous Products
Cobalt-based Catalyst

			Propylene/Propane				1-Butene/n-Butane			
Reactor			1	2	4	5	1	2	4	5
Nominal S, wt %			0.29	0.43	0.50	0	0.29	0.43	0.50	0
Experiment	H_2/CO	Pressure, kPa								
4-1	1.9	600	1.45	2.22	2.25	1.25	0.79	1.35	1.39	0.64
4-2	1.5	600	2.33	2.55	2.43	2.37	1.36	1.58	1.44	1.40
4-4	1.9	1100	0.62	1.18	0.05	0.61	0.19	0.60	—	0.23
4-5	1.5	1100	1.80	2.47	2.00	2.22	1.08	1.55	1.06	1.36
4-7	2.0	1600	0.41	1.59	1.29	0.82	0.13	0.97	0.69	0.39

For all conditions, ethylene/ethane ratios were negligible.

It has been shown (39,40) that the primary products of the FT reaction are α-olefins which may be hydrogenated in a consecutive step to give the corresponding paraffins. If this is the case, then it is interesting to note how sulfur affects the hydrogenation capacity of the catalyst. For all conditions the catalyst in which the sulfur was relatively well-distributed (reactor 2) consistently gave olefin/paraffin values greater than those obtained from the unsulfided catalyst. High values were also obtained in several experiments for the catalyst containing the most sulfur (reactor 4). This means that under certain conditions sulfur can reduce the hydrogenation of the primary olefinic product to paraffins. Variation of the olefin/paraffin ratio was also dependent on the process pressure, and it was highest at 600 kPa when compared to other pressures at a particular value of H_2/CO. Though it is difficult to justify, a more efficient hydrogenation took place at the intermediate pressure of 1100 kPa and a H_2/CO value of 1.9 rather than at 1600 kPa. The effect of sulfur and pressure was significant only when a H_2/CO ratio of 1.9 was used. The olefin/paraffin ratio was highest for H_2/CO equal to 1.5, and in this case the effect of sulfur and pressure was minimal. It is important to note here how the effect of sulfur relates to different process conditions.

Previous research by Roelen at Ruhrchemie (41) showed that the rate on a cobalt-based catalyst was independent of pressure between 20 to 101 kPa. The same result was found at USBM (42, 43) between 101 and 1500 kPa. As the apparent activation energy obtained by others (43) was approximately 84 kJ mol^{-1}, external diffusion was not controlling the reaction. Two conclusions may be tentatively drawn from the above observations. First, if the true order of reaction is zero the problems of external diffusion would not be present, and therefore external mass transport is not influencing our observations. Also, as shown in section 2, we have minimized the problems of internal diffusion by using small catalyst particles. Secondly, the surface of cobalt is probably well covered by chemisorbed reactants, and an Eley-Rideal type of mechanism, in which a gaseous molecule reacts with a chemisorbed specie, will not apply in this case. Either a surface step or product desorption could be rate limiting. Sakharov and Dokukina (44) have obtained a kinetic isotope effect by using $2D_2$ + CO and $2H_2$ + CO and by comparing the reaction rates at pressures of about 150 kPa. Values of 1.3 were obtained for the kinetic isotope effect, and the authors noted that this was incompatible with the mechanism in which desorption of growing hydrocarbon chains was the rate limiting step. The important step seems to be a surface step involving direct participation of hydrogen or some intermediate containing hydrogen. It must be noted that the conclusions made above regarding the zero order dependence of the reaction rate are tentative because the results from past work may have been influenced by transport effects.

Let us calculate an approximate turnover number (N) for the Fischer-Tropsch reaction. The turnover number is defined as the moles of a reactant consumed per surface mole of active material per second. A cobalt metal particle size of 11.5 nm was obtained by X-ray diffraction measurements on the used catalyst. This metal particle size corresponds to a metal dispersion (D), i.e. the fraction of surface cobalt atoms, of approximately 0.08. Assuming that after catalyst reduction all the cobalt on the support occurs as the metal, the following value of N_{CO} is obtained for the unsulfided catalyst in Experiment 4-1:

$N_{CO} = 2.0 \times 10^{-3}\ s^{-1}$ at 197°C and 600 kPa total pressure

This may be a conservatively low value as all the cobalt on the support may not be metallic. The value of N_{CO} for methanation at atmospheric pressure obtained by Vannice (45) on a 2% Co/Al_2O_3 catalyst ($\bar{D} = 0.08$) was $4.6 \times 10^{-4}\ s^{-1}$ after extrapolation to 197°C. Furthermore, Vannice (45) obtained a -0.5 order dependence on CO pressure. The two values of N_{CO} for FT and methanation thus seem to be close. However, when compared to other reactions such as hydrogenation of olefins where N at ambient conditions is about 1 s^{-1} (46), the Fischer-Tropsch reaction can be seen to be extremely slow.

Another interesting observation is the effect of sulfur, pressure and H_2/CO ratio on the distribution of condensed hydrocarbons. We will refer to Figures 3.1a, 3.1b, 3.2a, 3.2b, 3.3a, 3.3b, 3.4a, 3.4b and 3.5.

Figures 3.1a and b refer to results from Experiment 4-1 performed at 600 kPa pressure and a H_2/CO value of 1.9. Product distributions from reactors 1, 2, and 5 show a similar trend with one maximum at C_{13}; a distinct shoulder S_1 for reactor 5 and a slight shoulder for reactor 2 are present at C_{24}. The results from reactor 4, which contains the largest amount of sulfur, are quite different showing a bimodal distribution with one maximum at C_{13}, like the other reactors, a minimum at C_{19} and a second maximum at C_{23}. It appears that the shoulder S_1 of the curve in Figure 3.1a has grown in Figure 3.1b to give the second maximum at C_{23}; this increase in higher molecular weight products may be attributed to the larger quantity of sulfur in reactor 4. Results from Experiments 4-2 obtained at 600 kPa pressure but at a H_2/CO value of 1.5 are similar but not identical to the results described above. Products from reactors 1, 2, and 5 (Figure 3.2a) once again show one maximum at C_{12} and a shoulder S_2 at C_{25}. Results from reactor 4 (Figure 3.2b) are more complex with peaks at C_{11} and C_{18}, and a shoulder S_3 which seems to correspond to shoulder S_2 in Figure 3.2a. The nature of the distribution of the products from reactor 4 is complex in both Experiments 4-1 and 4-2.

Figures 3.3a and 3.3b refer to results from Experiment 4-4 performed at 1100 kPa and a H_2/CO value of 1.9. Reactors 1, 2, and 5 (Figure 3.3a) once again show similar results, but here they all give a bimodal distribution with the first maximum at C_{10}-C_{13}, a minimum at C_{16}-C_{18} and a second maximum at C_{21}-C_{22}. It is interesting to note that the minimum in the case of reactor 2 (0.43 wt % S) is not as sharp as that obtained with reactors 1 and 5. As the sulfur content increases to 0.5 wt % (reactors 3 and 4, Figure 3.3b) this minimum disappears and only one maximum at C_{21} is observed. The first maximum in Figure 3.3a seems to appear as shoulders S_4 and S_5 in Figure 3.3b. Once again, it seems that the products of reactors 3 and 4 are slightly heavier, i.e. the maximum at C_{21} has grown perhaps at the expense of the 1st maximum of reactors 1, 2, and 5. The product distribution from Experiment 4-5, which was also performed at 1100 kPa but at a H_2/CO value of 1.5, is quite different from Experiment 4-4. Reactors 1 and 5 show similar distributions (Figure 3.4a) with three maxima at C_{10}, C_{17} and C_{22}-C_{23}. The last maximum is more like a large shoulder. Products from reactors 2, 3, and 4 (Figure 3.4b) show similar trends with no sharp peaks and a broad distribution of heavier hydrocarbons.

Distribution of Condensed Products
Precipitated Cobalt-based Catalyst

T = 195°C, P = 600 kPa, SV = 217 V/V/h, H_2/CO = 1.9

Figure 3.1a

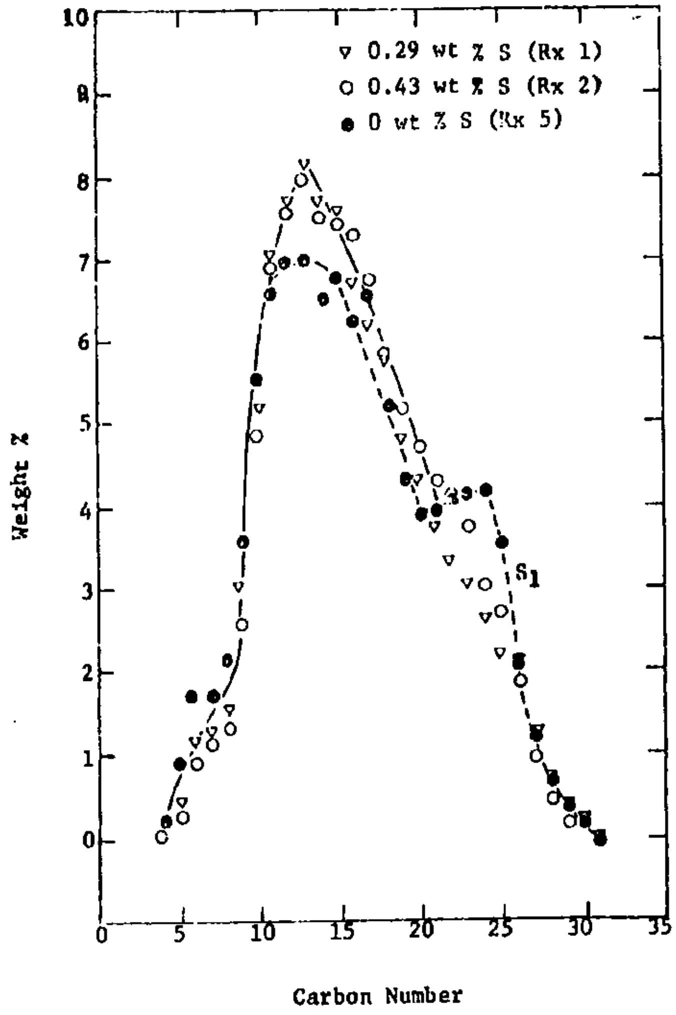
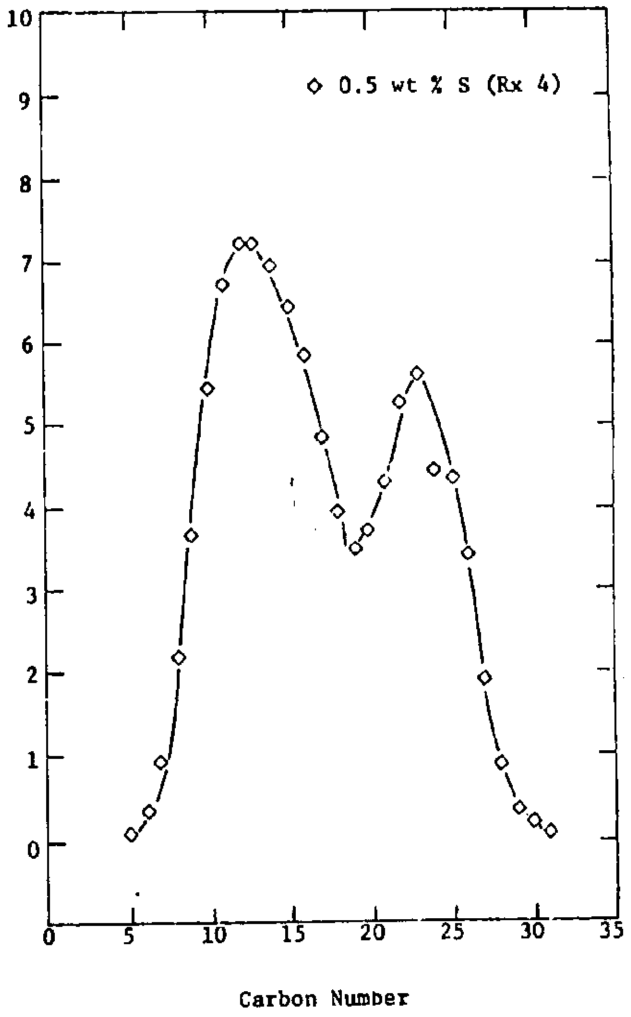


Figure 3.1b



Note: Rx = Reactor

Distribution of Condensed Products
Precipitated Cobalt-based Catalyst

T = 195°C, P = 600 kPa, SV = 204 V/V/h, H_2/CO = 1.5

Figure 3.2a

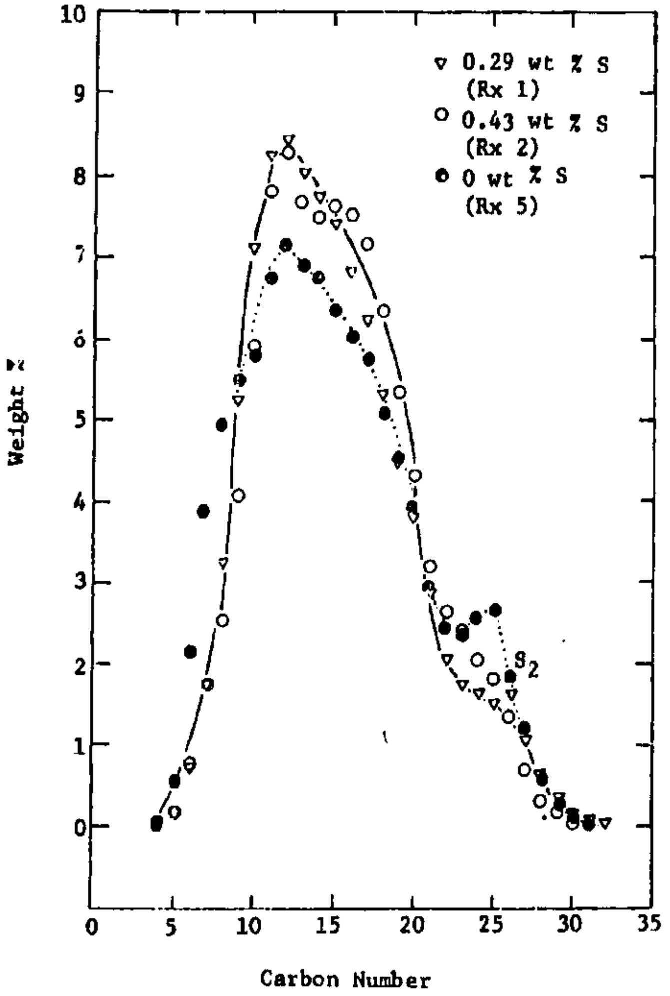
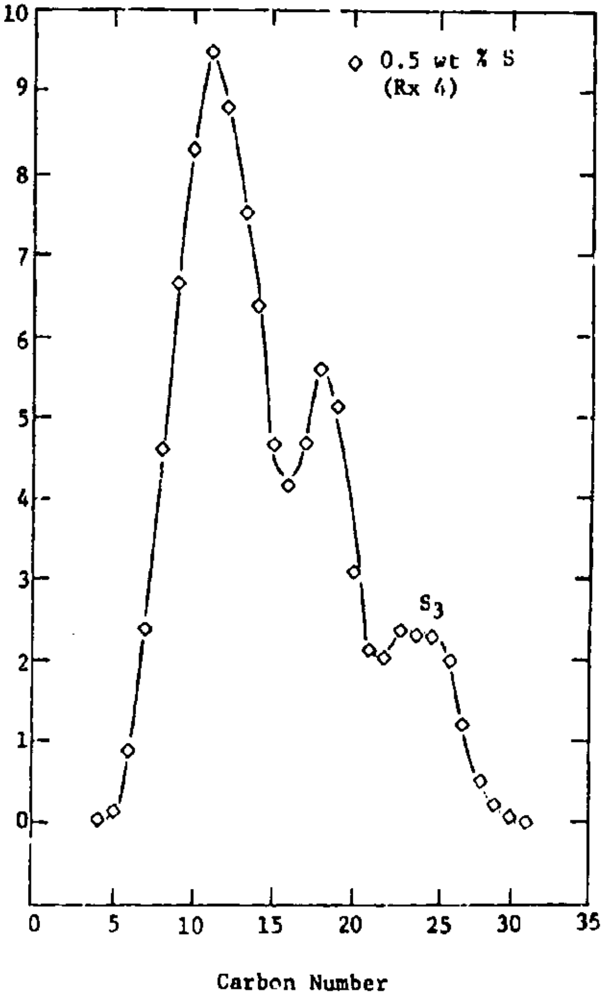


Figure 3.2b



Note: Rx = Reactor

Distribution of Condensed Products
Precipitated Cobalt-based Catalyst

T = 197°C, P = 1100 kPa, SV = 210 V/V/h, H_2/CO = 1.9

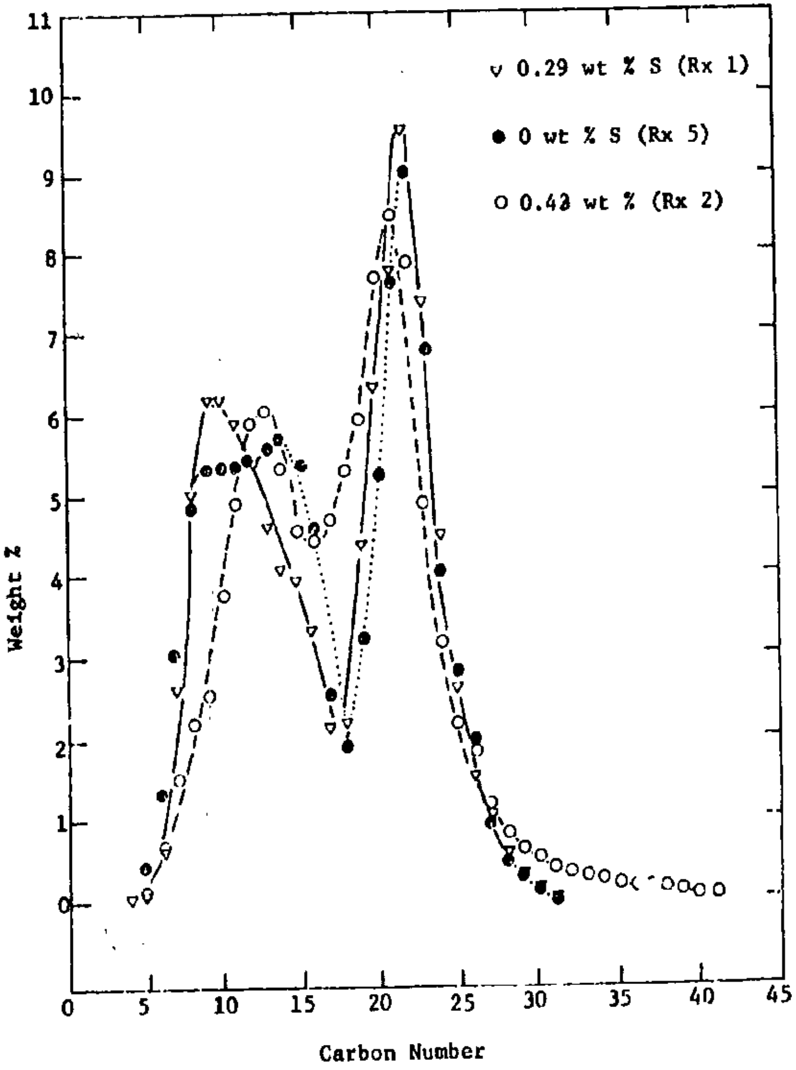


Figure 3.3a

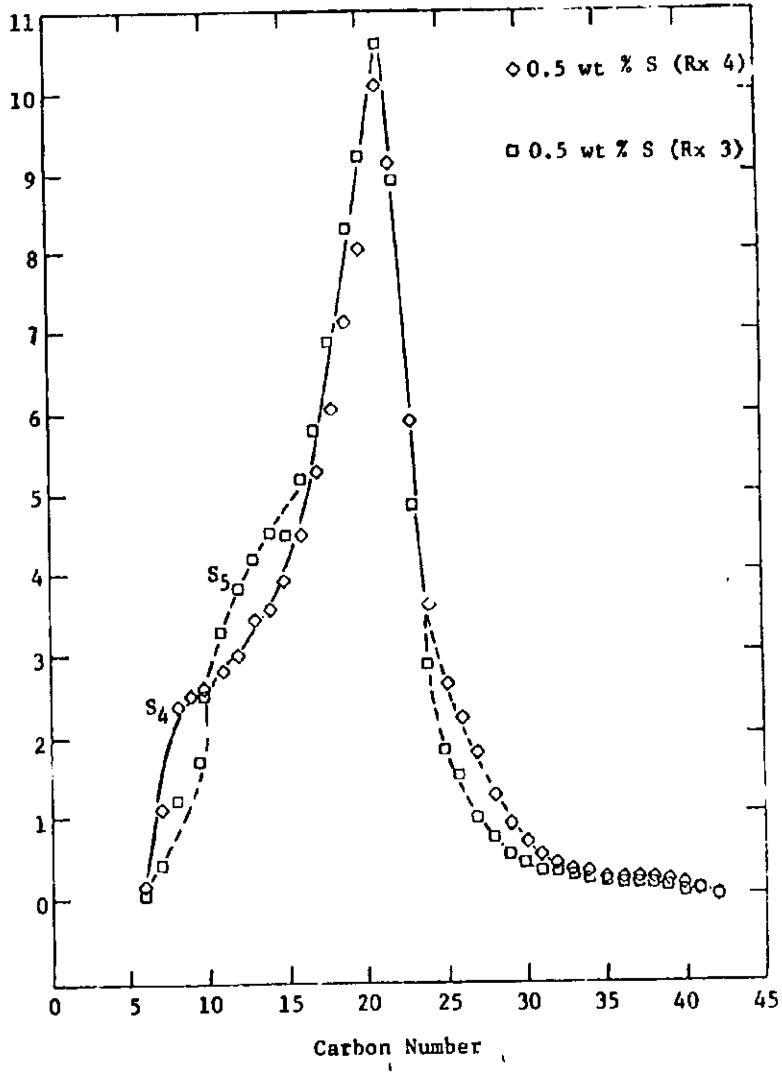


Figure 3.3b

Note: Rx = Reactor

Distribution of Condensed Products
Precipitated Cobalt-based Catalyst

T = 195°C, P = 1100 kPa, SV = 200 V/V/h, H_2/CO = 1.5

Figure 3.4a

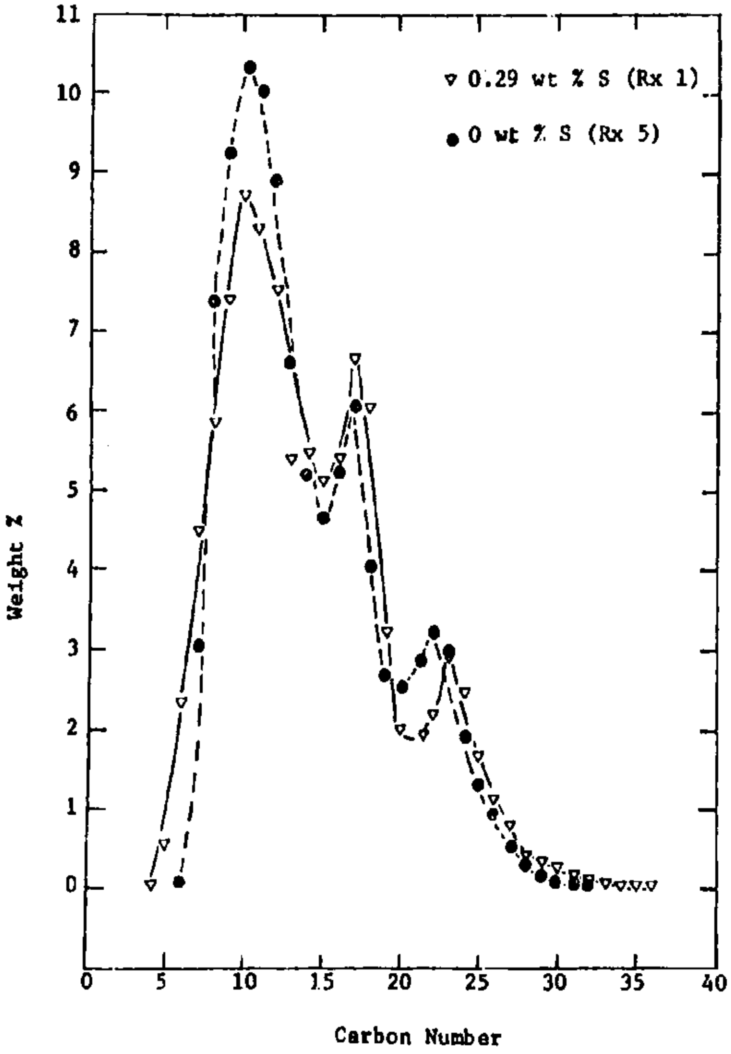
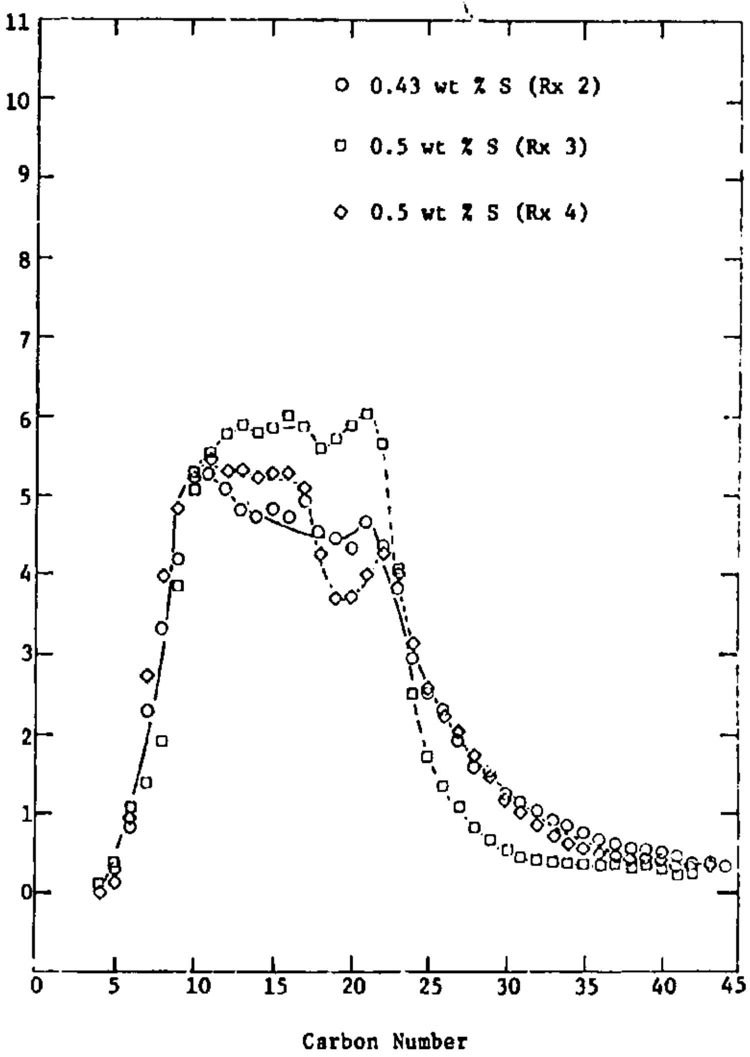


Figure 3.4b



Note: Rx = Reactor

Finally, Figure 3.5 refers to results from Experiment 4-7 performed at the highest pressure, 1600 kPa. Here all the reactors, 1, 2, 4, and 5, give an almost identical trend including the subtle but noticeable shoulder S_6 at about C_{25}. The initial maximum seems to be split at C_{11} and C_{18}; this is most evident for reactor 2 and is slightly different for the different reactors. This difference, however, is small. The important fact is that at the highest pressure similar amounts of heavy hydrocarbons are formed in all cases and the effect of sulfur on the carbon number distribution is small; i.e. the pressure effect dominates the sulfur effect. This is quite different from the results at 600 kPa and 1100 kPa.

Some important points regarding the results of the carbon number distributions are summarized below:

1. Bi-modal distributions are obtained at several conditions.
2. A peak or shoulder exists between C_{20} and C_{25}.
3. In experiments conducted at 600 kPa and 1100 kPa heavier hydrocarbon products are formed when larger amounts of sulfur are present in the catalysts.
4. At 1600 kPa, the effect of sulfur on the distribution is small.
5. Increasing the pressure tends to increase the formation of heavier products.

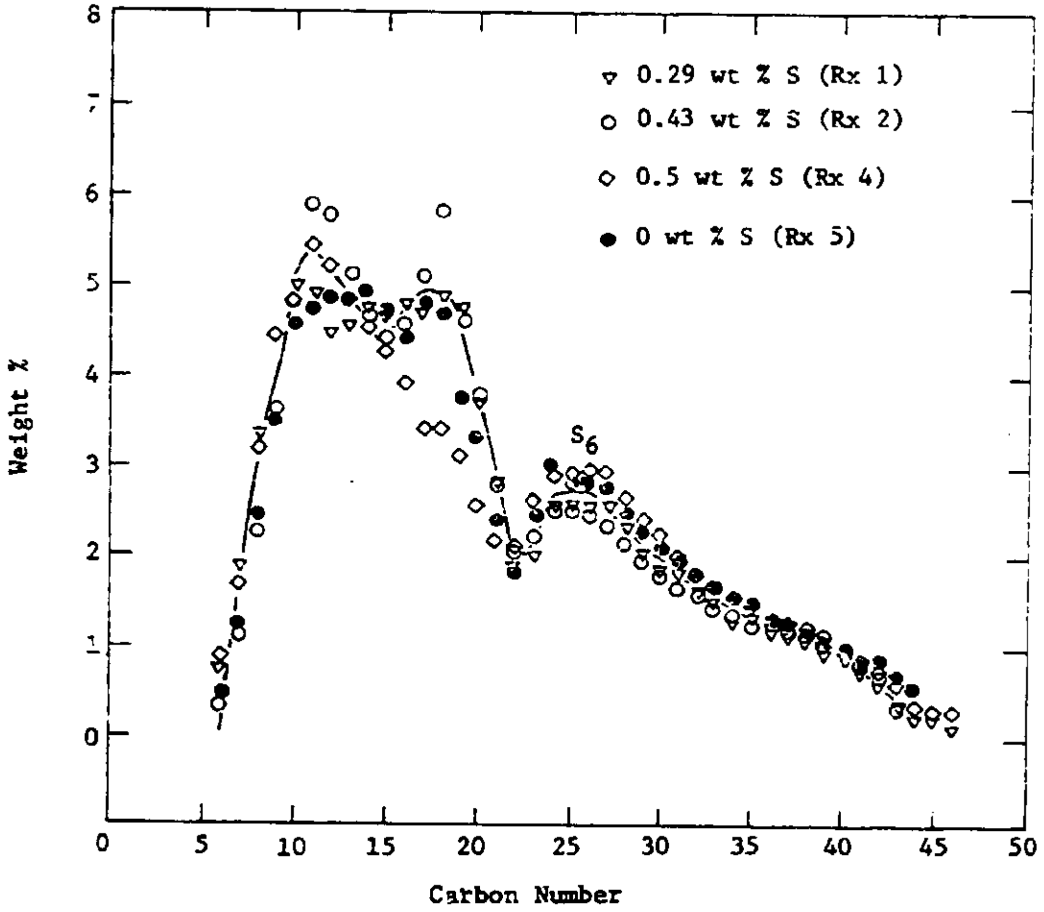
The mechanism of the FT synthesis has been stated to be similar to an oligomerization mechanism, and the chain growth may be due to the addition of CH_2 species (47), due to surface condensation with oxygenated surface species (43), or due to CO insertion type reactions (48). For such a mechanism the product distribution cannot have more than one maximum. The fact that bimodal distributions have been observed by us signifies that besides the primary oligomerization type process important secondary reactions must also affect the growth of hydrocarbon molecules. The more recent articles (39, 49, 50, 51) on FT synthesis have analyzed this point. Henrici-Olivé and Olivé (49) used the Schulz-Flory distribution law, which has been used to describe molecular weight distributions in oligomerization processes, to fit Fischer-Tropsch hydrocarbon data. The law was obeyed well only for carbon numbers between C_4 and C_{12}. As only a small amount of products heavier than C_{12} leave the reactor in the gas phase, their residence time is large, and hence they are most likely to be involved in secondary reactions. Pichler et al. (50) analyzed the change of growth rate of hydrocarbons and concluded that the concept of chain growth in one-carbon steps is insufficient to explain the construction of larger hydrocarbon molecules.

Since the pioneering work of Eidus and coworkers (52, 53), and Kölbel and Ruschenburg (54) on the role of olefins in FT synthesis, recent results (51) using C^{14}-tagged olefins have established the fact that olefins participate in the synthesis reaction to a considerable degree.

Figure 3.5

Distribution of Condensed Products
Precipitated Cobalt-based Catalyst

T = 197°C, P = 1600 kPa, SV = 209 V/V/h, $H_2/CO = 2.0$



Note: Rx = Reactor

It has also been established that α-olefins are the primary FT products (39), and that they are consequently hydrogenated to the respective alkane. Alkanes, after being desorbed, do not behave like their precursor alkenes and do not participate in the FT reaction (51). The C^{14} tracer studies, on Co : ThO_2 : kieselguhr catalyst, conducted by Schultz et al. (51) contained several important observations. It was found that the overall conversion of tracer olefins was over 90%. Though hydrogenation to paraffins constituted the principal reaction of olefins, other secondary reactions played an essential role. Olefins may crack, initiate a chain by forming a chemisorption complex which can grow further with CO and H_2, interact with other hydrocarbon chains which are growing on the catalyst, and, especially in the case of ethylene, terminate hydrocarbon chains growing on the catalyst. Perhaps the most important result is that this activity of olefins is not limited to ethylene, propylene and butene but is also seen for larger molecules such as 1-hexadecene. One intriguing conclusion by Schulz et al. is that 1- and 2-C atoms of 1-hexadecene seem to be transferred to other groupings growing on the catalyst. These reactions of olefins may take place after they have initially desorbed and then readsorbed in another part of the system. In our experiments negligibly small amounts of ethylene were observed. In comparison, relatively large quantities of propylene and 1-butene were obtained; in fact, depending on the experimental conditions, often more of the C_3 and C_4 olefins were formed than their respective paraffins. The rate of hydrogenation of ethylene to ethane is probably not very much greater than the corresponding rates for propylene and 1-butene. Therefore, more C_2H_4 could have been consumed in secondary reactions.

Hence we suggest that bi-modal distributions arise due to the presence of secondary reactions. It is interesting to see that in most of the cases studied here a peak or shoulder in the carbon-number distribution curve almost always occurred around C_{20} to C_{25}. This may mean that secondary reactions are most influencial near these points. In two cases (Figures 3.2b and 3.4a) the second maximum falls between C_{15} and C_{20}, but the same curves also have shoulders between C_{20} and C_{25}. Hence, the effect of secondary reactions may be dependent on reaction conditions.

Finally, let us rationalize the difference in the product distributions from some reactors in the same experiment. An examination of the distribution curves shows that reactor 5 (0 wt % sulfur) and reactor 1 (0.29 wt % sulfur) give results showing similar trends but which are different from those of reactors 3 and 4 (0.5 wt % S). The results from reactor 2 (0.43 wt % S) are either like those of reactors 1 or 4 depending on the experimental conditions. Closer examination of the curves shows that the results of reactor 4 differ because they usually contain heavier hydrocarbons than the products obtained from the unsulfided catalyst. For example, in the bi-modal curve in Figure 3.1b a second peak with a maximum at C_{23} is observed, whereas only a slight shoulder is evident near the same area in Figure 3.1a. This increase of heavier products, seen in Figure 3.1b, which leads to a bi-modal distribution is probably due to the effect of sulfur. A similar trend is seen in the results from other experiments except for the case when the reaction pressure was 1600 kPa. At this high pressure the effect of sulfur was negligible. It can be concluded that the product distribution is affected by the presence of sulfur and the experimental conditions. And the sulfur effect itself interacts with experimental parameters. Hence, a result on a catalyst with a certain amount of sulfur and at a certain experimental condition cannot be safely extrapolated to different experimental conditions or to catalysts containing different amounts of sulfur.

3.1.4 Summary

- The addition of up to 0.5 wt % (nominal) sulfur did not deactivate the catalyst.

- The selectivity to C_5+ products remained essentially independent of either sulfur addition or the experimental parameters used by us.

- However, the distributions of the condensed products were dependent on the presence of sulfur and on the experimental parameters. Under several conditions, bi-modal distributions were obtained.

- The presence of sulfur tended to increase the molecular weight of the condensed products at 600 and 1100 kPa. At 1600 kPa this effect of sulfur was not observed. However, increasing the pressure increased the molecular weight of the products.

- The olefin/paraffin ratio of C_3 and C_4 hydrocarbons was usually larger for the catalyst containing sulfur. However, at H_2/CO ratios of 1.5 the effect of sulfur or pressure on the olefin/paraffin ratios was minimal.

- The effect of sulfur interacts with process conditions. Hence, a result on a catalyst with a certain amount of sulfur and at a certain experimental condition cannot be safely extrapolated to different experimental conditions or to catalysts containing different amounts of sulfur.

3.2 Precipitated Iron-based Catalyst

3.2.1 Catalyst Pre-treatment and Sulfiding

Seven reactors were filled with 40 cm^3 (39.42 g) of 60 to 120 mesh 100 Fe : 21.8 Cu : 1.0 K_2CO_3 catalyst. The reactors, after being assembled on the unit, were flushed and then pressure tested with He. The pressure was reduced to atmospheric pressure and the temperature of the catalyst was increased to 225°C under flowing H_2+ CO (1:1) at a space velocity of 100 V/V/h. The catalyst was treated under these conditions for 24 h. The induction temperature was increased to 230°C, and the treatment was further continued for 24 h. Finally, the temperature was raised to 235°C, and the treatment was ended after a final induction period of 24 h. The reactors were then flushed with He before sulfiding.

Reactors 5, 6, and 7 were isolated from the gas manifold and kept under He, while the catalyst in reactors 1, 2, 3, and 4 was sulfided at 235°C and atmospheric pressure. A 2:1 mixture of H_2:CO containing 150 ppm was used at a space velocity of approximately 400 V/V/h. No H_2S was detected coming out of the reactors. Table 3.6 gives the nominal sulfur levels calculated on weight % of unreduced catalyst and as mg S per g of Fe.

Table 3.6

Nominal Sulfur Levels on the Iron-based Catalyst Used in Run 5

	Nominal Sulfur Level	
Reactor	as wt % of unreduced catalyst	as mgS/g Fe
1	0.08	1.4
2	0.24	4.3
3	0.24	4.3
4	0.40	7.2
5	--	--
6	--	--
7	--	--

As nominal sulfur levels do not give complete information regarding the amount of sulfur on the catalyst, a detailed longitudinal sulfur gradient analysis was done (Table 3.7). At the end of run 5 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 3.7, 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 after all carbon had been removed, i.e. the wt % reported is not masked by the wax on the spent catalyst.

Table 3.7

Longitudinal Sulfur Distribution in Catalyst Beds for Run 5

Section	Reactor 1 % S by wt	Reactor 2 % S by wt	Reactor 3 % S by wt	Reactor 4 % S by wt
1	2.39	5.59	5.44	13.50
2	0.10	0.17	0.24	5.27
3	0.04	0.06	0.05	0.77
4	0.05	0.08	0.04	0.15
5	0.03	0.02	0.06	0.04
6	0.03	0.02	0.03	0.04
7	0.02	0.04	0.03	0.04
8	0.02	0.04	0.02	0.02
9	0.01	0.01	0.05	0.06
10	0.02	0.02	0.03	0.01
11	0.02	0.01	0.02	0.01
12	0.01	0.03	0.01	0.02
13	0.02	0.03	0.01	0.03
14	0.02	0.06	0.01	0.01

In all cases the inlet portion of the bed contains most of the sulfur. In reactor 4 approximately 25% of the catalyst bed at the reactor inlet has most of the sulfur. This observation will be used in future discussions. Sulfur in reactors 5, 6, and 7 was negligibly small throughout the bed, nominal sulfur content being < 0.02% S by wt.

3.2.2 Experiments Performed

Before discussing the complete run, let us list the experiments in the order that they were performed (Table 3.8). After each experiment, the catalyst was kept overnight in flowing He at the same temperature and pressure used in the experiment. The following table gives the experimental conditions and duration of each test: