SUMMARY

Coal, an abundant natural resource, may have to play a significant role for the production of transportation fuels and thus help to overcome the problems created by diminishing petroleum reserves. The most developed process for producing aliphatic liquid fuels from coal is the Fischer-Tropsch synthesis which is based on catalytically reacting CO and H_2 obtained via coal gasification. The discovery and development of selective catalysts that give high space-time yields of required fuels is essential for improving this process. Moreover, the contemplated feed gases obtained from coal gasification contain sulfur compounds which have been acknowledged as catalyst poisons. Little work has been done to date regarding the effect of sulfur on Fischer-Tropsch catalysts. It is important to study the influence of sulfur on these catalysts as activity, selectivity, and catalyst longevity are all crucial factors for future catalyst development.

The scope of our work was to investigate the effect of adding small quantities of sulfur to materials which may be useful as catalysts for the Fischer-Tropsch synthesis. Materials in the fully sulfided form were also to be tested as potential catalysts. The main objective was to ascertain whether the introduction of small amounts of sulfur to a catalyst could enhance the selectivity to liquid hydrocarbons without impairing the overall activity. A secondary, though important, objective was to check if certain catalysts could function with sustained high activity in the presence of sulfur even without marked improvements in product selectivity. Thus, certain materials could be identified as having potential for use as sulfur-resistant catalysts for the H_2-CO reaction.

After conducting a detailed literature search, several traditional and non-traditional Fischer-Tropsch catalysts were tested, with and without the introduction of sulfur as H_2S, in a tubular packed bed reactor system. Of the catalysts studied, only alumina-supported Ru was severely poisoned by sulfur. Evidence was obtained that alkali-promoted precipitated cobalt-based and iron-copper catalysts have the potential to withstand deactivation by sulfur to a certain extent. Sulfided Co-Mo/Al_2O_3 and Ni-W/Al_2O_3 catalysts, and KOH promoted MoS_2 were also found to be active CO hydrogenation catalysts. It is therefore felt that these results could provide a basis for developing sulfur-resistant Fischer-Tropsch catalysts.

The effect of sulfur on catalytic selectivity depended on the type of catalyst and experimental conditions. There was no effect of S on the selectivity of the precipitated Fe-Cu catalysts. However, for the Co-based catalyst, though the presence of sulfur did not markedly alter the overall amounts of C_4- and C_5+ hydrocarbons produced, it did change the distribution of the condensed C_5+ products. For example, under certain conditions unexpected bi-modal distributions were obtained, and the observed changes indicated that the addition of sulfur increased the molecular weight of the products. The addition of sulfur to alkalized Co-Mo/Al_2O_3 and Ni-W/Al_2O_3 catalysts enhanced the selectivity to condensed products. Furthermore, the molecular weight of the condensed products obtained with sulfided, alkalized Co-Mo/Al_2O_3 was greater than that of the condensed products obtained with unsulfided, alkalized Co-Mo/Al_2O_3.

It is indeed important to note that non-metallic, non-traditional catalysts such as MoS_2 promoted with KOH, and sulfided or unsulfided Co-Mo/Al_2O_3 catalysts with or without alkali, were found to be active for hydrocarbon synthesis. However, tungsten-based catalysts, which are sometimes used interchangeably with Co-Mo/Al_2O_3 catalysts in other processes such as hydrotreating, were not as active. These results indicate that certain non-metallic surface structures could lead to sites active for the Fischer-Tropsch synthesis even in the presence of large amounts of sulfur. In fact, the presence of sulfur may even be necessary for catalytic action.

The best selectivity for liquid hydrocarbons, useful for transportation fuels, was obtained on the 1% Ru/Al_2O_3 catalyst. For example, at 240°C, 3.1 MPa (450 psi) pressure, a space-velocity of 200 V/V/h, and a H_2/CO ratio equal to 2, the Ru catalyst showed a H_2+CO conversion of 95% with 98% of the reacted CO producing C_5 to C_{25} aliphatic hydrocarbons. It was also found that though S poisoned Ru/Al_2O_3, it tended to increase the formation of heavy hydrocarbons. In fact, at experimental conditions where unsulfided Ru produced large quantities of methane, the sulfided catalyst still showed high selectivity to C_{5}+ products. It was also observed that the activity of the poisoned Ru catalysts could be dramatically improved by increasing the reactant pressure from 2 to 3 MPa. Unlike Co and Fe, Ru-based catalysts may be used at pressures much above 1.5 to 2 MPa (217.5 to 290 psi), hence our results could be useful for working with Ru-based catalysts in the presence of sulfur.

Our results indicate that the interaction of sulfur with alkali promoters may be important for product selectivity and resistivity against poisoning. Further research on the action of promoters may be one way of developing improved Fischer-Tropsch catalysts.

Besides such interactions, we also found that there were significant interactions of process conditions with different sulfided and unsulfided catalysts. In fact, the carbon number distribution of the Fischer-Tropsch products varied widely and was a complex function of catalyst type, process conditions, and sulfur effects. It is therefore important to note that for such a complex reaction catalyst evaluation at a single set of experimental parameters would be inconclusive. Also, in studies aimed at producing liquid transportation fuels, the reaction should be carried out under experimental conditions that allow the condensed product selectivity pattern to develop fully. Hence integral, rather than differential, reactor operation becomes necessary. Though this magnifies problems associated with transport phenomena, certain measures were taken by us to minimize the influence of such physical artifacts on our kinetic investigations.

1. INTRODUCTION

Since the availability of petroleum derived fuels is projected to decrease between now and the end of this century, the U.S. must find ways of optimizing the utilization of other fossil fuels among the principal energy consuming sectors. One principal cause for concern is the current unavailability of alternate sources of fuels for transportation. Other fuel intensive sectors, such as electric power generation, can depend on coal or nuclear fuel to provide the energy if petroleum based fuels become scarce. The transportation sector, on the other hand, is projected to need liquid fuels such as jet and diesel fuels containing high concentrations of paraffins because combustion requirements in current engines limit the content of aromatics in the fuel (Table 1.1). Hence, excluding gasoline, the required fuels for transportation could be made synthetically from shale oil or tar sands but probably not out of coal liquefaction products. This is due to the high concentration of aromatic and naphthenic compounds present in coal liquids which are not economically amenable for conversion to paraffin based fuels. It is imperative, however, that methods be found to use our vast reserves of coal to produce transportation type fuels. The most developed process for producing paraffins from coal is the Fischer-Tropsch (FT) process. This process is based on the gasification of coal which produces CO and H_2. These gases can then be catalytically combined to give products which are predominantly aliphatics. Table 1.2 shows the possible uses of the different products that can be obtained from the FT synthesis.

Table 1.1

Fuel Characteristics (1)

	Approximate Range of Carbon Numbers	Aromatics, Vol. %
Motor Gasoline (Unleaded)	C_4-C_{11}	37-54
Aviation Turbine Fuel		
JP-4	C_5-C_{15}	< 25
JP-5	C_{10}-C_{15}	< 25
Diesel Fuel	C_9-C_{21}	< 25

Table 1.2

Uses of Fischer-Tropsch Products

Products	Uses
CH_4, C_2-C_4 Hydrocarbons	Industrial & Household Fuel, Chemical Feedstock
Naphtha, C_5-C_{10} (Low Octane Number)	Gasoline Blending, Chemical Feedstock
Middle Distillates, C_9-C_{20} (High Cetane Number)	Jet and Diesel Fuel
Medium Gas Oil, C_{16}-C_{25}	Marine Diesel Fuel
Heavy Gas Oil, C_{22}+	Lube Oil, Waxes, Feedstock for Cat-Cracking

With the Fischer-Tropsch process, it is important to obtain efficient conversion of H_2 and CO at sufficiently high space-velocities to given economic space-time yields of products. Hence, the key to improvement lies in the development of active catalysts which are highly selective. In addition to improving activity and selectivity, Fischer-Tropsch catalysts must be made resistant to deactivation from poisons such as sulfur compounds ordinarily present in synthesis gas obtained via coal gasification. It is generally acknowledged that sulfur compounds readily poison nickel, cobalt, iron, and ruthenium based catalysts which are normally used for the synthesis of hydrocarbons from CO and H_2 (2). The early German work of Fischer and Tropsch (3), and Fischer and Dilthey (4) stressed the need for scrupulous removal of sulfur compounds in reactant gas streams. Fischer (5) in 1935 cited a practical upper limit for sulfur concentrations of 1 to 2 mg/m^3 of synthesis gas.

Under ERDA-sponsorship [contract #(46-1)-8008] Exxon Research and Engineering Company undertook to investigate the effect of sulfur on catalysts active for the FT synthesis. The program called for a study of catalysts containing 0 to approximately 0.5 wt % sulfur and also for the evaluation of catalysts in sulfide form. The specific objectives of the project were to establish the existence of any sulfur promotional effects leading to improved selectivity and increased yields of liquid products, and to check if certain catalysts showed resistance to sulfur poisoning.

The program was divided into two phases. The first phase consisted of a detailed literature search which has been discussed in the Phase I report (Exxon/GRU.1KWA.76) and elsewhere (6). As a result of our extensive review of the literature on Fischer-Tropsch synthesis, it was determined that comparatively little data have been reported regarding the effects of sulfur compounds on Fischer-Tropsch catalysts. This is mainly due to the general acknowledgment that sulfur compounds are deleterious to the synthesis and hence should be removed from the reactant synthesis gas. However, eleven research groups in four different countries and over a period of 45 years have reported that the interaction of trace quantities of sulfur with different Fischer-Tropsch catalysts can lead to beneficial selectivity changes or sustained high activity or both. A summarized account of this past research has been tabulated in Appendix A.

The second phase of the program involved the experimental study of the effect of sulfur on various catalysts. This report addresses itself to the results and discussion of the experimental research. The apparatus and experimental techniques are discussed in Section 2 which also includes a short account of the reproducibility of results and problems associated with transport phenomena. The results on the various catalysts are described in Section 3, a general discussion is given in Section 4, and recommendations are given in Section 5.

2. EXPERIMENTAL

2.1 The Fischer-Tropsch Catalyst Test Unit

The flow diagram of the Fischer-Tropsch catalyst test unit is shown in Figure 2.1, and it indicates all the essential parts of the unit except the different types of valves, safety features, and thermocouple placements.

The unit was made of stainless steel and was used for the simultaneous operation of up to seven Alonized[1] stainless steel reactors, all at the same temperature, pressure, H_2/CO ratio and space-velocity. The reactors could be used simultaneously with different catalysts, if required, and with varying catalyst pretreatment and amount of sulfiding. The unit could be used at pressures up to 3 MPa.

Hydrogen was passed through a Deoxo unit to remove traces of oxygen and then through a molecular sieve trap to eliminate water vapor. Carbon monoxide was also passed through a molecular sieve trap. The H_2S/H_2 mixed gas, however, was used for sulfiding without going through any purification steps. Finally, provisions were also made to admit helium and air into the unit. Air was necessary due to the following reason. As the Fischer-Tropsch catalyst used under reducing conditions, may have been pyrophoric, it could not be suddenly exposed to air. Hence, before dismantling the reactors after an experimental run, the catalyst was first carefully treated at room temperature with small amounts of air diluted with an inert gas. The gas flow rate into each reactor was set and measured via the procedure outlined in Appendix B. The gas flow rate out of each reactor was obtained either at point X with a soap bubblemeter or with the wet-test meter. As shown in Figure 2.1, the condensible products from each reactor were recovered in two stages. Waxes and heavy hydrocarbons were collected in the first stage whereas the lighter products were trapped in knockouts immersed in an ice bath. Residual gases were separated and sent to the saturator. When required, these gases were analyzed chromatographically.

The reactor furnace (Figure 2.2) consisted of an Alonized[2] copper pipe, and each reactor was placed in one of the seven equidistant slots provided around the pipe. Three electrical heaters were stacked in the hollow center of the pipe, and the temperature of each heater was controlled separately with a Barber-Colman Model 20 solid-state controller. Besides placing thermocouples in the copper pipe, one thermocouple was embedded in the catalyst, in each reactor, to record its temperature with the help of a potentiometer and a multi-point recorder. The operation of several reactors in parallel enabled us to compare simultaneously the performance of different catalysts under identical conditions, or to evaluate simultaneously the performance of identical catalysts with different pretreatments or different amounts of sulfur.

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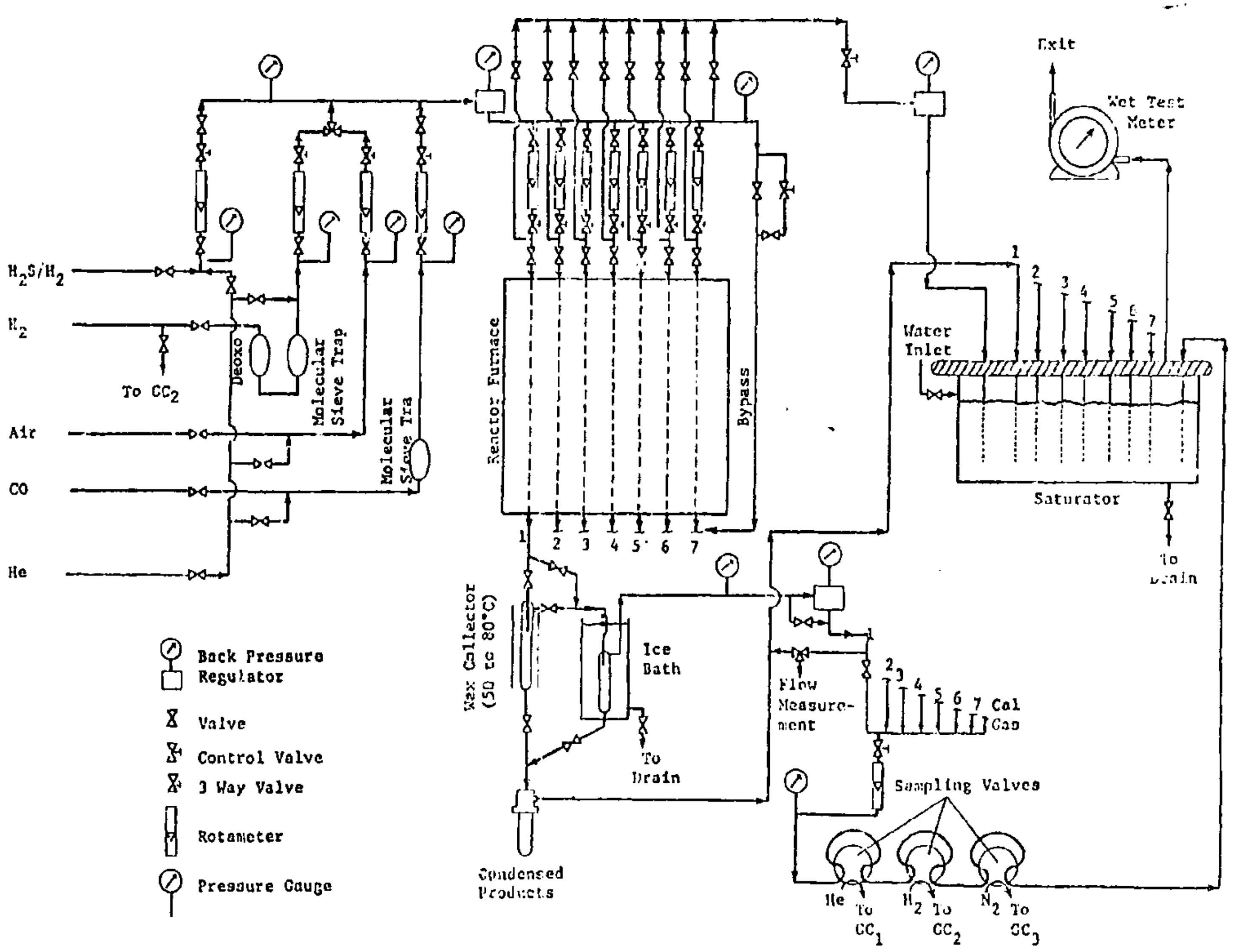
[1] A process which coats the stainless steel with aluminum and alumina. It renders the reactor walls inert for FT reactions and, more importantly, for interaction by sulfur compounds.

[2] Alonizing in this case prevents oxidation of the copper.

Figure 2.1

Fischer-Tropsch Catalyst Test Unit



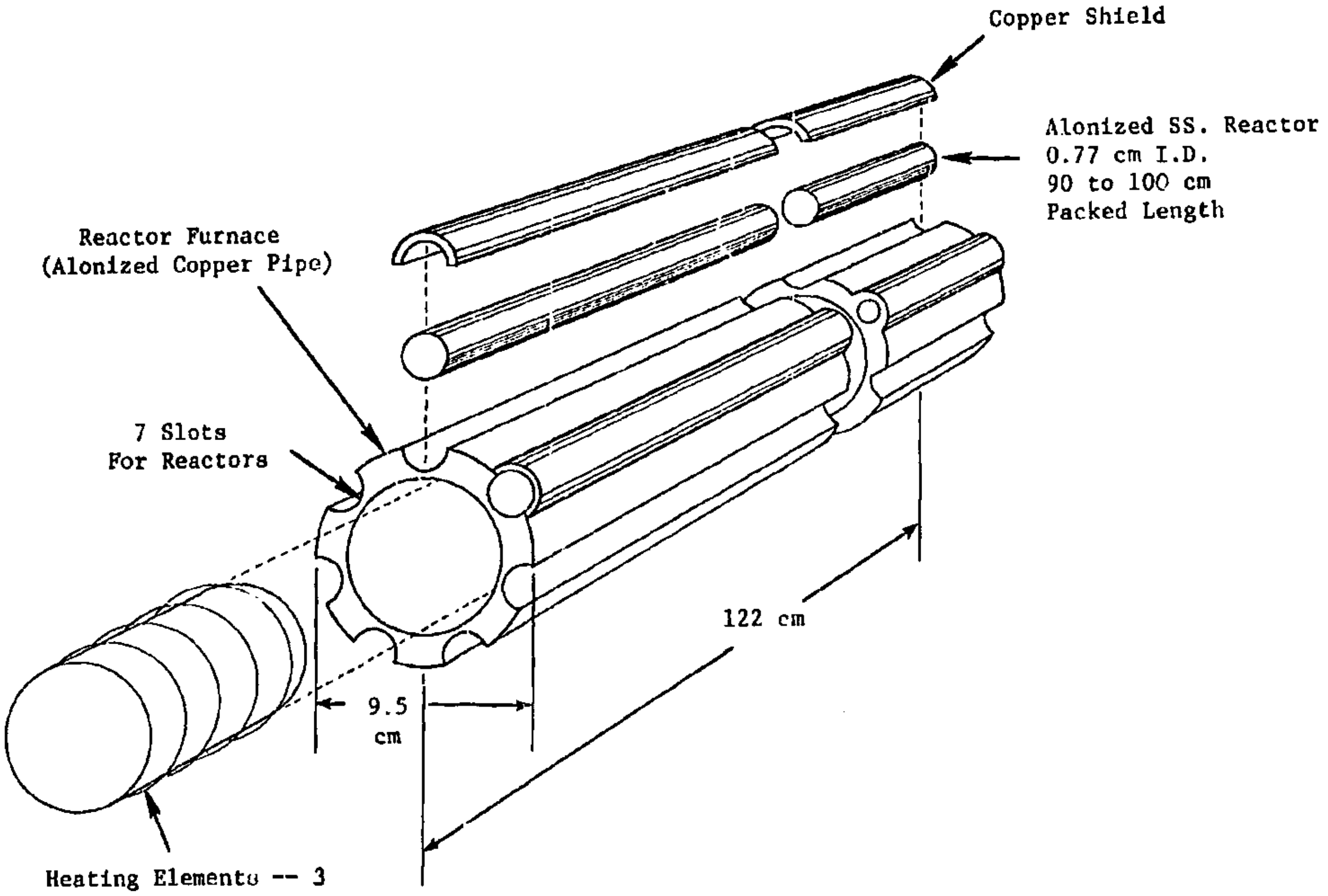


Figure 2.2

A Tubular, Packed Bed Multiple Reactor System

2.2 Analytical Procedures

Exit gases from each reactor were analyzed using a chromatographic train consisting of the following units:

- Hewlett Packard F & M 720 - thermal conductivity detector - 3.05 m Poropak Q column - CO and CO_2 detection - H_2 as carrier gas. Hydrogen was used instead of He to prevent interference by H_2 in the product stream on CO chromatograms. Carrier gas flow rate = 80 cm^3/min, column temperature = 40°C.

- Hewlett Packard F & M 720 - thermal conductivity detector - 1.8 m molecular sieve 5A column - H_2 detection - N_2 as carrier gas. Carrier gas flow rate = 80 cm^3/min, column temperature = 40°C.

- Perkin Elmer 3920 (a) flame ionization detector - 3.05 m n-octane on Poracil C - gaseous hydrocarbon detection, CH_4 to C_4 hydrocarbons - He as carrier gas. Carrier gas flow rate = 40 cm^3/min, column temperature = 40°C.

  (b) flame photometric detector - 1 m Triton X + 2 m Carbopak column - sulfur compound detection - He as carrier gas. Carrier gas flow rate = 18 cm^3/min, column temperature = 40°C.

The carbon number distribution of the condensed products was obtained with a Perkin Elmer 900 chromatograph using a flame ionization detector and a 3.05 m column containing 10% SP 2100 on 80-100 mesh Supelcoport. The column was temperature programmed from 60°C to 350°C at 8°C/min and held at 350°C. Helium, flowing at 30 cm^3/min, was used as the carrier gas.

The weight % of sulfur on the catalysts was obtained via the high temperature combustion Dietert technique (ASTM method D1552). This method could not be used for the alumina-supported Ru catalysts because the chlorine on the alumina support interfered with the test. The sulfur content on the Ru catalysts was obtained via an in-house combustion-gravimetric technique using a Parr bomb similar to the ASTM method E257.

2.3 Catalysts

The catalysts used and the corresponding run numbers are given in the following table:

Table 2.1

Test Catalysts

Catalyst	Run Number
Precipitated Cobalt-based	
1. 100 Co : 15.9 ThO_2 : 92.9 kieselguhr : 1.96 K_2CO_3	4
Precipitated Iron-based	
2. 100 Fe : 21.8 Cu : 1.0 K_2CO_3	5
Molybdenum-based	
3. 3% Co-oxide + 11% MoO_3/Al_2O_3	6
4. 3% Co-oxide + 11% MoO_3/Al_2O_3 + 3.45% K_2O	6
5. MoS_2 + 3% KOH	7
Tungsten-based	
6. 3% Ni-oxide + 10% WO_3/Al_2O_3	7
7. 3% Ni-oxide + 10% WO_3/Al_2O_3 + 3.3% K_2O	7
8. 10% WO_3/Al_2O_3 + 3.42% K_2O	7
Ruthenium-based	
9. 1% Ru/Al_2O_3	8
10. 1% Ru/Al_2O_3 + 10% KOH	8

Catalysts 1 to 8 were prepared by Harshaw Chemical Company; catalysts 9 and 10 were prepared by Engelhard. The preparation techniques used are given below.

Catalyst 1 [Harshaw Sample No. 689A-6-1-10]

Kieselguhr	Celite FC Grade (S.N. 689A-1-1-4)
Nitric Acid	Baker and Adamson Reagent
Cobalt Nitrate	Harshaw Flake 453-009-68
Thorium Nitrate	Mallinckrodt A.R.
Soda Ash	Harshaw Light
Water	Deionized

Johns-Mansville Celite (FC Grade) was acid treated by digesting for five hours at 70-80°C with a nitric acid solution. After washing with deioniz water, the material was calcined at 650°C for two hours. This material (S.N. 689A-1-1-4) was used as the substrate.

A boiling soda ash solution and a boiling kieselguhr slurry were added simultaneously to a boiling Co-Th nitrate solution, and the pH was adjusted between 7.5-8.0. After filtering, the cake was washed with deionized water at room temperature. The cake was dried at 110°C and treated with K_2CO_3 in a water-alcohol solution. The K_2CO_3 was based on the available Co by analysis. After drying, the catalyst was mixed with 1/2% graphite. Slugs 1.3 cm in length were made with a RB-2 tabletting machine and were subsequently crushed and sized to 60-100 mesh granules.

Catalyst 2 [Harshaw Sample No. 689A-2-6]

Ferrous Chloride	Mallinckrodt
Ferric Chloride	Mallinckrodt
Cupric Chloride	Baker Reagent
Sodium Carbonate	Harshaw Light
Potassium Carbonate	Pure
Water	Deionized

A chloride solution was prepared to contain 75 parts Fe^{++}, 25 parts Fe^{+++}, and 20 parts Cu. The solution was then heated to 70°C and mixed with a hot (90-100°C) soda ash solution. The mixing was carried out as rapidly as possible and was limited only by the large quantities of foam generated. At the final pH (7.2-7.5) the precipitate had changed from a dark brick red thick past to a thin black metallic slurry.

The precipitate was then filtered and washed in a washing type filter press using deionized water until the effluent had a chloride level slightly lower than tap water. A potassium carbonate solution was then incorporated in the wet press cake. After drying, 60-100 mesh granules were prepared.

Catalysts 3 and 6 were commercial Harshaw catalysts HT-400 and W-0404, respectively. Catalysts 4 and 7 were prepared by impregnating the corresponding sized catalysts with a solution of K_2CO_3. Catalyst 8 was similarly prepared using Harshaw W-0801. The MoS_2 catalyst was obtained commercially from Climax Molybdenum as a technical grade reagent and impregnated with KOH at Harshaw Chemical Company.

The 1% Ru/Al_2O_3 was obtained from Engelhard in the reduced form. It was prepared according to the procedure used to manufacture their proprietary commercial supported Ru catalysts. Catalyst 10 was obtained by impregnating the reduced Ru catalyst with KOH.

2.4 Reproducibility of Results

In this subsection problems encountered during experimentation will be discussed, and the reproducibility of the data will be established. All detailed experimental conditions, results and calculations are given in Appendix D.

In run 4, reactors 5, 6, and 7 contained sulfur-free catalyst and hence were identical. During Experiment 4-1, reactor 6 gave a very low conversion. This was thought to be due to catalyst bypassing. The reactor furnace was opened, and reactor 6 was tapped with a hammer. Results from reactor 6 improved during Experiment 4-2, but the conversions were still lower than those from reactors 5 and 7. Reactor 6 was tapped once more, and a slight improvement was noted again during Experiment 4-3. It was concluded that (a) gas was bypassing the catalyst in reactor 6, and (b) this situation could improve as the run proceeded. The last conclusion was justified when reactors 5 and 6 gave identical results in the last experiment (4-8). Catalyst bypassing has been known to be a problem in Fischer-Tropsch synthesis. Waxes that form during the synthesis or during catalyst induction could cause the small catalyst particles to adhere together and hence cause a poor gas distribution within the bed (2). Similar problems regarding catalyst bypassing were not encountered in other runs.

Another problem which may arise during Fischer-Tropsch synthesis is that of reactor plugging. We encountered this problem only once. Reactor 3 plugged during Experiment 4-6; this caused the gas flows into the other reactors to fluctuate during the course of this experiment, and the accuracy of the data was impaired.

Finally, large fluctuations of gas flow rate were sometimes observed, for example, in reactor 6 during Experiment 6-1 and in reactor 5 during Experiment 8-10. Results obtained under such conditions will not be discussed.

The average range ($\bar{R}$) and standard deviation (σ') of the measured values were calculated from replicate sets of data for runs 4, 5, and 6. The standard deviation was obtained by dividing $\bar{R}$ by a factor which was dependent on the number of observations in a subgroup. In our case, the number of observations in a subgroup was 2 and the factor was 1.128 (7). Table 2.2 indicates the values of $\bar{R}$ and σ' and thus the reproducibility of the experimental results. The standard deviation of the various measured conversions and yields was often well below 10% of the measured value. This proves that the data obtained during experimentation were reliable.

Analyses of exit gases (H_2, CO, CO_2, CH_4 - C_4 hydrocarbons) were accurate within 10%. The largest inaccuracy was in measuring the reactants flowing <u>into</u> each reactor, and in ensuring that the flow and the H_2/CO ratio remained constant throughout the run. The result that was most dependent on the above errors was the calculation of selectivity: CO converted to C_5+ hydrocarbons. This value was obtained by subtracting the amount of CO converted to gaseous products (i.e. CO_2, CH_4 - C_4 hydrocarbons) from the total amount of CO consumed in the reaction. Unlike cobalt and iron

Table 2.2

Reproducibility of Results

	Run 4		Run 5		Run 6	
	$\bar{R}$ %	σ'%	$\bar{R}$ %	σ'%	$\bar{R}$ %	σ'%
CO_2-free contraction, %	1.6	1.4	1.6	1.4	4.5	3.9
Hydrogen conversion, %	1.1	1.0	4.3	3.8	5.4	4.8
Carbon monoxide conversion, %	2.3	2.0	0.6	0.5	2.2	1.9
CO converted to gaseous products[1]; μmol/min	11.3	10.0	3.4	2.9	3.0	2.7
CO converted to C_5+ hydrocarbons, μmol/min	4.9	4.3	6.3	5.6	*	*
Selectivity: % CO converted to CH_4	13.8	12.2	3.8	3.4	2.9	2.6
% CO converted to CO_2	12.9	11.4	3.9	3.5	4.6	4.1
% CO converted to C_5+ hydrocarbons	3.4	3.0	4.8	4.3	*	*

$\bar{R}$: average range for the normalized difference between replicate measurements

σ': standard deviation of the measured (or calculated) values

A sample calculation of $\bar{R}$ and σ' is given in Appendix C.

[1] CH_4, C_2 - C_4 hydrocarbons and CO_2

*see test

Run 4: reactors 5 and 7 were compared except for experiment 4-8 when reactors 5 and 6 were compared (see text)

Run 5: reactors 5 and 7 were compared

Run 6: reactors 6 and 7 were compared

Run 7: identical catalysts were not used

Run 8: the results will be discussed separately during analysis of the data on ruthenium-based catalysts

catalysts, Co-Mo and W-based catalysts produced significant quantities of gaseous products, compared to condensed products, hence the calculation of the value of CO converted to C_5+ hydrocarbons was dependent on the subtraction of two large numbers causing the errors for the selectivity to C_5+ hydrocarbons to be increased. The value of zero for this selectivity in the tables in Appendix D should probably read 0+%. There is hence a large uncertainty when values of the selectivity lie between 0 and 10% (asterisk in Table 2.2). There is a similar large uncertainty when the conversion of H_2 or CO is between 0 and 10%; this occurs with some catalysts in runs 7 and 8.

Finally, an example will be given to show the reproducibility of two separate runs. Experiments 4-4 and 4-6 were performed under similar conditions. And though problems were encountered during the latter experiment, it is interesting to compare the results of reactor 5 for these two experiments. It must be noted that Experiment 4-5, with a different H_2/CO ratio, was performed in between Experiments 4-4 and 4-6, and the results of Experiment 4-5 are quite different from those of 4-4 and 4-6. The good comparability of results (Table 2.3) on similar experiments done two days apart with a totally different experiment done in between shows that the data are capable of being reproduced and are quite meaningful.

Table 2.3

Comparison of Results from Reactor 5

Catalyst: Cobalt-based

The experiments were performed two
days apart, and the experimental
conditions were quite similar.

Experiment	4-4	4-6
Nominal S, wt %	0	0
Pressure, kPa	1100.00	1100.00
Space-velocity, V/V/h	217.00	201.00
Inlet H_2 flow, cm^3/min	119.36	111.82
Inlet CO flow, cm^3/min	61.52	55.54
Reaction temperature, °C	196.00	195.00
Avg. contraction, %	91.56	91.99
CO_2-free contraction, %	94.10	94.54
H_2 converted, cm^3/min	115.36	107.09
H_2 converted, µmol/min	4651.42	4318.06
H_2 conversion, %	96.65	95.77
CO converted, cm^3/min	58.81	55.19
CO converted, µmol/min	2371.12	2225.45
CO conversion, %	95.58	99.36
H_2 usage ratio	0.66	0.66
Gaseous products, µmol/min		
CH_4	125.10	114.51
C_2H_6	21.97	20.80
C_2H_4	0.00	0.00
C_3H_8	20.21	23.25
C_3H_6	12.46	5.01
n-C_4H_{10}	12.11	11.89
1-C_4H_8	2.78	0.64
CO_2	184.84	172.17
Total hydc. gas, µmol/min	194.66	176.13
CO converted to gas, µmol/min	511.55	463.29
CO converted to hydc. gas, µmol/min	326.70	291.12
CO converted to C_5+ hydrocarbons		
µmol/min	1859.56	1762.15
cm^3/min	46.12	43.70
Selectivity, % CO converted to:		
C_5+	78.42	79.18
CH_4	5.27	5.15

2.5 Transport Phenomena

The intrusion of artifacts such as intraparticle (internal), interphase (external), and interparticle mass and heat transport effects during the investigation of a heterogeneously catalyzed reaction can completely mask the intrinsic kinetics of the reaction (8 , 9). Often, the different behavior of an identical catalyst for the same reaction in different reactor systems (10) may be attributed to the influence of transport effects. Recognizing that transport phenomena can disguise results and lead to inaccurate conclusions, one must use available theoretical criteria to check design parameters for possible interference by the artifacts mentioned above. Generally, the relative importance of effects fall in the order: interparticle heat transport > interphase heat transport > intraparticle mass transport > interphase mass transport > intraparticle heat transport (11, 12).

The Fischer-Tropsch synthesis is difficult to study for several reasons. The high exothermicity of the reaction can lead to large temperature gradients. Often low space-velocities, large residence times, are required, and the particle Reynold's number (Re_p) is hence small; $Re_p < 5$. As the reactants, H_2 and CO, combine to give high molecular weight condensible products, there is significant gas contraction, and the molar gas flow rates at the entrance and exit of the reactor may be different by as much as an order of magnitude. The Reynolds number would hence be different in different parts of the reactor giving rise to different heat and mass transfer coefficients which could lead to non-uniform heat and mass transfer effects (13). Moreover, deviations from plug-flow could also arise. At the temperatures and pressures used, the pores of the catalyst contain liquid hydrocarbon products (14). The diffusivity of reactants into the liquid-filled pores would be approximately three orders of magnitude smaller than vapor phase diffusion, thus increasing the problems of intraparticle mass transport. In catalytic reactions it is assumed that mass transport into pores takes place by molecular diffusion. This assumption is generally valid. However, in certain cases when gases react to give liquids or vice versa, a large pressure gradient could arise between the pore-mouth and the end of the pore. In the case of FT synthesis one can speculate that a higher reactant gas pressure at the pore-mouth could give some resistance to the flow of liquid products out of the pores, and this could lead to the occurrence of secondary reactions. A detailed analysis of the reverse case, liquid → gas, using D'arcy's Law, is given elsewhere (15).

One common approach for minimizing transport effects is to adopt differential (low overall conversion) conditions by manipulating the space-velocity, pressure, and temperature. This can be readily done for most reactions. Experimental parameters, however, critically affect product selectivity in the Fischer-Tropsch synthesis. For example, a FT study at 1 atm pressure and high space-velocity conditions which shows some formation of methane and light hydrocarbon gases as the main products would not correctly represent the reaction carried out at 15 atm and a low space-velocity which gives condensed products. As stated before, FT synthesis is useful for obtaining middle distillate fuels, and hence reaction conditions must be used to give hydrocarbons up to a carbon number of about C_{25}, i.e. to allow the condensed product selectivity pattern to develop fully. Integral operation hence becomes necessary, and the problems of transport phenomena are magnified. The effects of physical artifacts have never been sufficiently analyzed for FT synthesis, and except for the data of Anderson, Karn, and Shultz (16) little mention of their importance has been found in the FT literature. Table 2.4 gives some of the results of Anderson et al. (16) on reduced and nitrided fused iron catalysts.

Table 2.4

Variation of Activity with Particle Size (16)

Particle Size Radius, cm	Reduced catalysts Activity *	Nitrided catalysts Activity *
0.151	40	75
0.116	54	77
0.0508	105	156
0.0225	185	228
0.0135	210	222

* Here, activity is defined as cm^3 (NTP) of H_2 + CO converted/gFe/h at 240°C, 2.16 MPa, and space-velocity = 300 V/V/h.

The above table indicates that activity measurements on catalyst particles larger than about 0.027 cm were influenced by intraparticle diffusion. Calculations by Shultz et al. (14) based on a simplified model indicate that the effective depth of the catalyst pore is only 0.01 to 0.04 cm.

Using criteria which have been recently proposed to check for transport effects in heterogeneous catalysis (11, 17 to 21) we shall discuss conditions under which FT synthesis, studied in a tubular plug-flow reactor, may not be significantly influenced by heat and mass transfer.

Assuming there is no strong product inhibition (2), the Weisz-Prater (17) criterion for internal diffusion may be used to obtain catalyst granule size for operation without problems associated with internal diffusion:

$$\text{Damköhler number for diffusion} = Da_{II} = \frac{R_0^2 r}{C_s D_e} \leq 1 \qquad [1]$$

From our work the rate of reaction (r) $\approx 2 \times 10^{-6}$ mol $s^{-1}cm^{-3}$ of catalyst. As mass transfer through the pore involves dissolution and diffusion of reactant gases through liquid hydrocarbons, the concentration (C_s) was obtained from solubility data (22, 23), and the bulk diffusivity (D) was obtained via the Wilke-Chang equation (24, 23); $C_s = 10^{-5}$ mol cm^{-3} and $D = 2 \times 10^{-4}$ cm^2s^{-1}. The effective diffusivity (D_e) may be obtained by reducing D by a factor of 10 to allow for the porosity and tortuosity of the catalyst; $D_e = D/10$ (9). The particle radius (R_p) may be calculated from equation [1]:

$$R_p \leq [\frac{C_sD_e}{r}]^{1/2}$$

$$R_p \leq 0.01 \text{ cm}$$

The effective particle diameter (d_p) should not be greater than 0.02 cm. This value can be favorably compared to the experimental observation given in Table 2.4 and also to the calculation of Shultz et al. (14). Much of the previous FT work has been done on considerably larger catalyst particles; Dry et al. (25) used particles of 0.3 to 0.4 cm diameter, Eidus et al. (26) used particles sized 0.4 x 0.4 cm, and Anderson and co-workers usually used particles with a diameter of 0.2 to 0.3 cm. This indicates that much of the previous work on Fischer-Tropsch synthesis was influenced by internal diffusion. In our work particles between 60 to 120 mesh size (0.025 cm to 0.013 cm) were used. Due to the small particles and low gas flow rates used in our work the values of Re_p are low:

$$0.1 \leq Re_p \leq 0.3$$

At such low Re_p, values of particle Sherwood numbers (Sh_p) and hence mass transfer coefficients (k_m) are small and are not known accurately. For example, at stationary conditions Miyauchi et al. (27) obtained Sh_p equal to 9.4, whereas at $Re_p \approx 0.1$, Sh_p values as low as 10^{-3} have also been obtained (28, 29).

The Hudgins criterion (18) may be used to obtain the minimum value of k_m required in order that external mass transfer does not dominate. The gas concentration (C_o), obtained at 1.5 MPa pressure and 240°C, is 3.6×10^{-4} mol cm^{-3}. As the order of reaction (n), to at least a first approximation (23), with respect to the concentration of synthesis gas is one, the criterion becomes:

$$\frac{rd_p}{k_mC_o} \leq 0.3 \qquad [2]$$

$$k_m > 3.7 \times 10^{-4} \text{ cm s}^{-1}$$

Gas phase diffusivity was calculated via the Gilliland equation (30) at 1.5 MPa pressure and 200°C; $D \simeq 0.07\ \mathrm{cm^2\ s^{-1}}$.

Therefore, $Sh_p = \frac{k_m d_p}{D} \geq 9.7 \times 10^{-5}$

The above value of Sh_p is less than the values given in the literature for $Re_p \simeq 0.2$. Hence, the effect of external mass transport will not be important.

It should be noted that gas-liquid mass transfer was assumed to take place in the catalyst pores whereas interphase transport was assumed to occur via gas phase diffusion. Furthermore, if the reaction order with respect to any reactant is zero then the problems of intraparticle diffusion with respect to that component is reduced, and the problem related to interphase diffusion would not arise.

The use of small granule sizes is also helpful in avoiding intraparticle and interphase heat transport effects. Anderson's criterion (19) can be used to check the former effect.

$$\text{Damköhler number for conduction} = Da_{IV} = \frac{\Delta H R_p^2 \bar{r}}{\lambda T_s} \leq 0.75 \frac{T_s R_g}{E} \qquad [3]$$

where:

ΔH = exothermic heat of reaction = 209 kJ $\mathrm{mol^{-1}}$
R_g = gas constant = 8.31 J $\mathrm{mol^{-1}K^{-1}}$
λ = thermal conductivity of the catalyst particle
$\simeq 4 \times 10^{-4}$ J $\mathrm{s^{-1}cm^{-1}K^{-1}}$ (9)
T_s[1] = surface temperature of the catalyst $\simeq$ 513 K
R_p $\simeq$ 0.01 cm

$$\text{LHS } (2 \times 10^{-4}) < \text{RHS } (3.8 \times 10^{-2})$$

The criterion is obeyed, and hence intraparticle heat effects will not be important.

Just as in the case of Sh_p, the values of the particle Nusselt number (Nu_p) at low Re_p and hence the heat transfer coefficient (h) are small and are not known accurately. For example, Kunii and Suzuki (29), and Nelson and Galloway (28) give values of Nu_p between 5×10^{-3} and 5×10^{-2} for $Re_p \simeq 0.1$. Gunn and De Souza (31), however, note that large errors could exist in measured values of Nu_p at $Re_p < 1$ due to the severe influence of axial dispersion. At low Re_p, Nu_p measured by Gunn and DeSouza approached a limiting value of 10. In our analysis of interphase

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[1] assumed in the calculation to be close to the bulk temperature (T_b)

heat transport, we will use Mears' criterion (11) to obtain the minimum value of h, and hence Nu_p, required in order that external heat transfer does not influence the reaction.

$$\left| \frac{\Delta H R_p r \cdot}{h T_b} \right| \leq \frac{0.15\ R_g T_b}{E} \qquad [4]$$

$$h \geq 1.1 \times 10^{-3}\ J\ s^{-1} cm^{-2} K^{-1}$$

The thermal conductivity (k_g) of the gas mixture [$H_2/CO = 1$] = 1.3×10^{-3} $J\ s^{-1} cm^{-1} K^{-1}$.

Therefore,

$$Nu_p = \frac{h d_p}{k_g} \geq 10^{-2}$$

This required value is easily obtained for $Re_p = 0.2$ according to the postulates and observations of Gunn and De Souza (31) but may not be obtained from the results of other experiments (29). Hence, it is difficult to ascertain the problem of interphase heat transport precisely. Recently, however, Wakao (32) argued that the low values of Sh_p or Nu_p reported in the past were due to erroneous assumptions. His analysis showed that in the range of $Re_p = 0$ to 1, Sh_p or $Nu_p > 1$. This result agrees favorably with that of Miyauchi et al. (27), and Gunn and De Souza (31), and indicates that our experiments are free from external transport problems. In any case, the minimum required value of h, $10^{-3}\ J\ s^{-1} cm^{-2} K^{-1}$, is small, and external temperature gradients, if present, would be small.

When reactors are operated in the integral mode the problems of interparticle transport (i.e. radial and longitudinal transport effects) are particularly difficult to control. Radial mass transport effects are usually not as serious as radial temperature gradients which, if neglected, can cause the reaction rate at the reactor axis to be substantially different from that at the wall (33). This can also drastically affect product selectivity. For an exothermic reaction such as the FT synthesis, radial temperature gradients in laboratory packed bed reactors can be a major problem because high axial temperatures could lead to excessive methane formation and carbon deposition. Furthermore, longitudinal (axial) dispersion effects and back-mixing can also distort reactor performance when high conversions are sought (34).

In addition to providing a good reactor furnace or other heat transfer medium such as boiling Dowtherm, two techniques used to maintain isothermal operation are to dilute the catalyst with an inert substance and to reduce the diameter of the reactor. A substance which may be inert by itself for the FT reaction e.g. kiesleguhr, may act differently in conjunction with an active catalyst; moreover, problems of catalyst bypassing become more severe with catalyst dilution, and hence we did not add inert solids to dilute our catalysts. Also as 20 to 50 cm^3 of catalyst was to be used, the smallest internal reactor diameter that could be used without causing the reactor to be unmanageably long was 0.77 cm ID (3/8" OD tube). The Mears' criterion (11) to check for the significance of radial temperature gradients is

$$\left| \frac{\Delta H d_t^2 r(1-\varepsilon)}{k_{er} T_w} \right| \leq \frac{1.6\ R_g T_w/E}{1 + 8/Bi_w} \qquad [5]$$

where:

d_t = internal tube diameter = 0.77 cm
T_w = wall temperature ≃ 513 K
ε = bed void fraction ≃ 0.5
k_{er} = radial effective thermal conductivity of catalyst bed
Bi_w = wall Biot number = $\frac{h_w d_t}{k_{er}}$
and h_w = heat transfer coefficient at the wall

For our conditions, a conservative value of k_{er} is given by $\frac{k_{er}}{k_g} = 5$ (35); therefore $k_{er} = 6.5 \times 10^{-3}$ J s^{-1}cm^{-1}K^{-1}. A conservative value of h_w may be taken to be approximately 0.2 J s^{-1}cm^{-1}K^{-1} (36). Hence, $Bi_w = 2.5$.

For equation [5]

$$\text{LHS } (3.7 \times 10^{-2}) \leq \text{RHS } (6.2 \times 10^{-2})$$

The above criterion is just barely obeyed for a reactor with a d_t value of 0.77 cm. Larger values of d_t, often greater than 1 cm, have been used frequently in the past (25, 26, 37) possibly resulting in large radial temperature gradients.

Though a small value of d_t is necessary to avoid radial temperature gradients when studying exothermic (endothermic) reactions, the ratio d_t/d_p should not be less than 10, or wall effects could become serious (20). Wall effects occur due to the fact that the packing is more open near the wall, and therefore the fluid velocity is larger there than at the reactor axis. This could lead to a lower conversion near the wall, and hence the apparent activity of the bed would be lower. In our case d_t/d_p = 39, and therefore wall effects will be negligible. It is interesting to note that though Dry et al. (25), Eidus et al. (26), and Karn et al. (37) used d_t values greater than 0.8 cm, the particle sizes used were also large, and hence the ratio d_t/d_p was less than 10, and wall effects could have been present.

The effects of longitudinal dispersion of heat and mass can be important. The low flow rates and small catalyst particles used would cause the axial Peclet numbers for thermal (Pe_{hz}) and mass (Pe_{mz}) transport to be small, and this could result in problems associated with longitudinal temperature and concentration gradients.

$$Pe_{mz} = \frac{ud_p}{D_z} \qquad Pe_{hz} = \frac{u\rho C_p d_p}{k_{ez}}$$

where:

u = superficial velocity = 0.75 cm s^{-1}

D_z = axial dispersion coefficient -- assume equal to D

ρ = gas density = 4×10^{-3} g cm^{-3}

C_p = heat capacity of gas at constant pressure = 2.76 J $g^{-1}K^{-1}$

k_{ez} = axial effective thermal conductivity - assume equal to k_{er}

$$Pe_{mz} = 0.21 \qquad Pe_{hz} = 0.03$$

As $Pe_{mz} > Pe_{hz}$, axial thermal dispersion problems will be greater.

Mears' criterion (20) will be first used to check for axial mass dispersion effects.

$$\frac{L}{d_p} > \frac{20n}{Pe_{mz}} \ln \frac{C_{initial}}{C_{final}} \qquad [7]$$

where:

L = packed bed length = 90 cm

Even if a high conversion of 95% is assumed, criterion [7] is easily obeyed, and axial mass dispersion will not affect the reaction.

The criterion attributed to Young and Finlayson (21) for axial heat dispersion at the reactor inlet is

$$\frac{(\Delta H) d_p r}{(T_i - T_w) u \rho C_p Pe_{hz}} << 1 \qquad [8]$$

where:

T_i = gas temperature before entering the reactor = 300 K

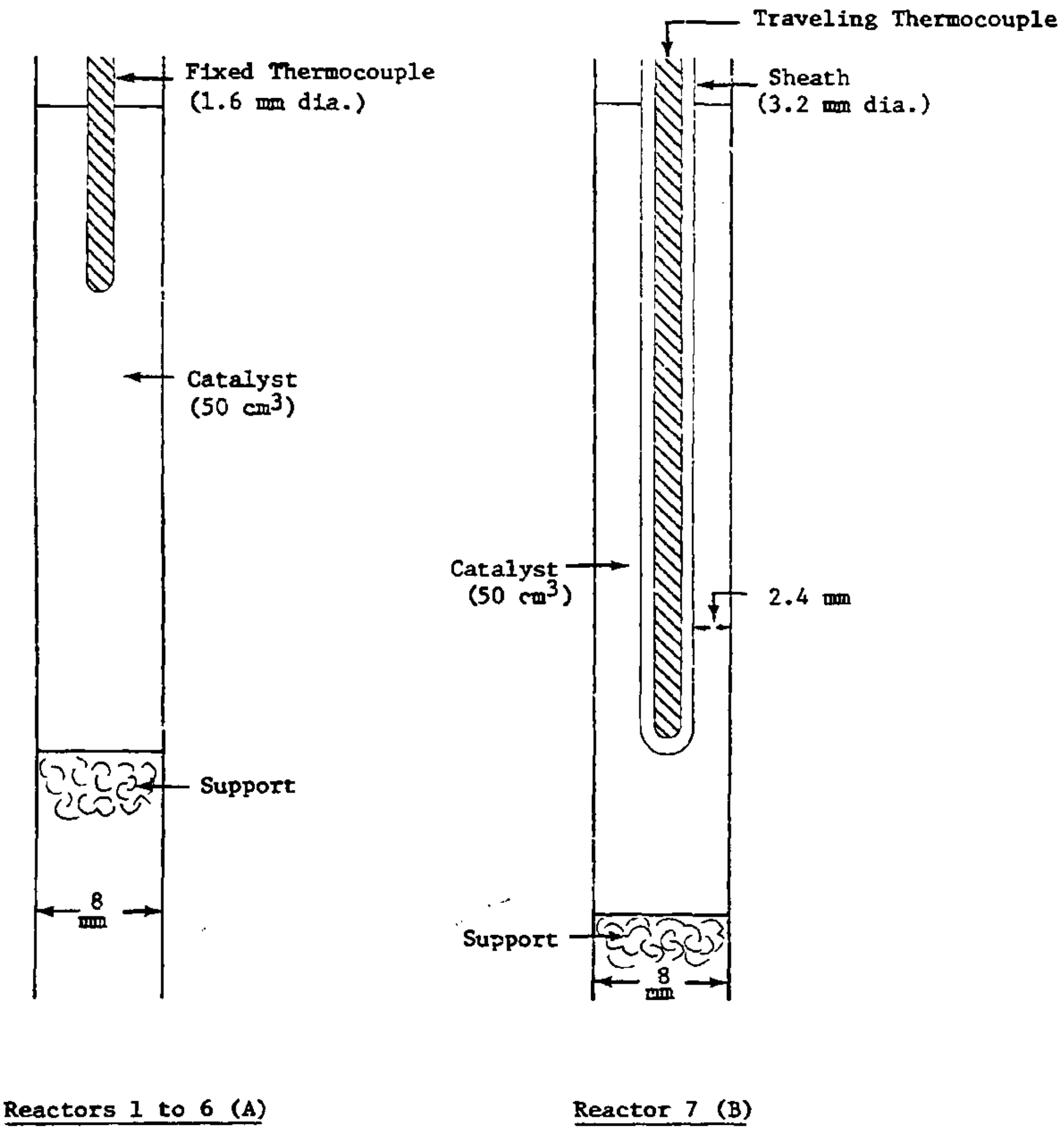
LHS = 0.2

Criterion [8] is obeyed but only by a factor of 5. Experimental measurement of the temperature along the axis of the packed bed is necessary to demonstrate the presence or absence of significant axial heat dispersion.

Figure 2.3 shows the thermocouple placements in the various reactors for run 4 with the cobalt-based catalyst. The traveling thermocouple in reactor 7 was used to check for any longitudinal temperature fluctuations in the bed, especially during the beginning of the experiment when hot spots

Figure 2.3

Thermocouple Placements in Run 4



could develop. NO such hot spots were found in Experiments 4-1 to 4-7 when the catalyst temperature was maintained at about 198°C. The temperature profile along the length of the bed for the experiments varied usually by ± 2°C. The maximum deviation of temperature was about 10°C in the beginning of the run and about 5°C after the run had progressed for about 1/2 h.

Figure 2.4 shows the thermocouple placements in the various reactors for run 5 with the iron-based catalyst. Once again, the traveling thermocouple in reactor 6 was used to check for any longitudinal temperature fluctuations in the bed. The hottest part of the reactor was approximately 5 to 10 cm below the catalyst inlet, and the extent of the hot zone was not more than 5 cm. The deviation in temperature depended on the reaction temperature. In Experiments 5-7 to 5-12 when the reaction temperature was 240°C or less, the temperature deviation of the hot zone was not more than 5 to 10°C. At reaction temperatures of 250 to 260°C, the increase in temperature was about 15°C or less. At the highest temperature used, 270°C, the temperature rise was 25°C. In all cases, the temperature profile along the length of the bed, excluding the 5 cm long hot zone, was quite flat with a maximum variation of ± 2°C.

It is felt that the experiments in run 4 (excluding Experiment 4-8) and in run 5 were not influenced by longitudinal temperature gradients. Traveling thermocouples were not used in other runs.

It can also be deduced from our experiments that radial temperature gradients were insignificant. Reactors (B) containing the 3.2 mm diameter sheath for the traveling thermocouple (Figures 2.3 and 2.4) have a reduced effective reactor radius. The path for radial heat transport is hence smaller, and heat transfer across the bed would be facilitated. If radial temperature gradients were present, they would be more predominant in reactors (A) fitted with the stationary 1.6 mm diameter thermocouples.

If large radial temperature gradients were present, the axial temperature would be much larger than the reactor wall temperature, and the following results may be expected:

a. Larger quantities of CH_4 and CO_2 would be produced in reactors A than in reactor B.

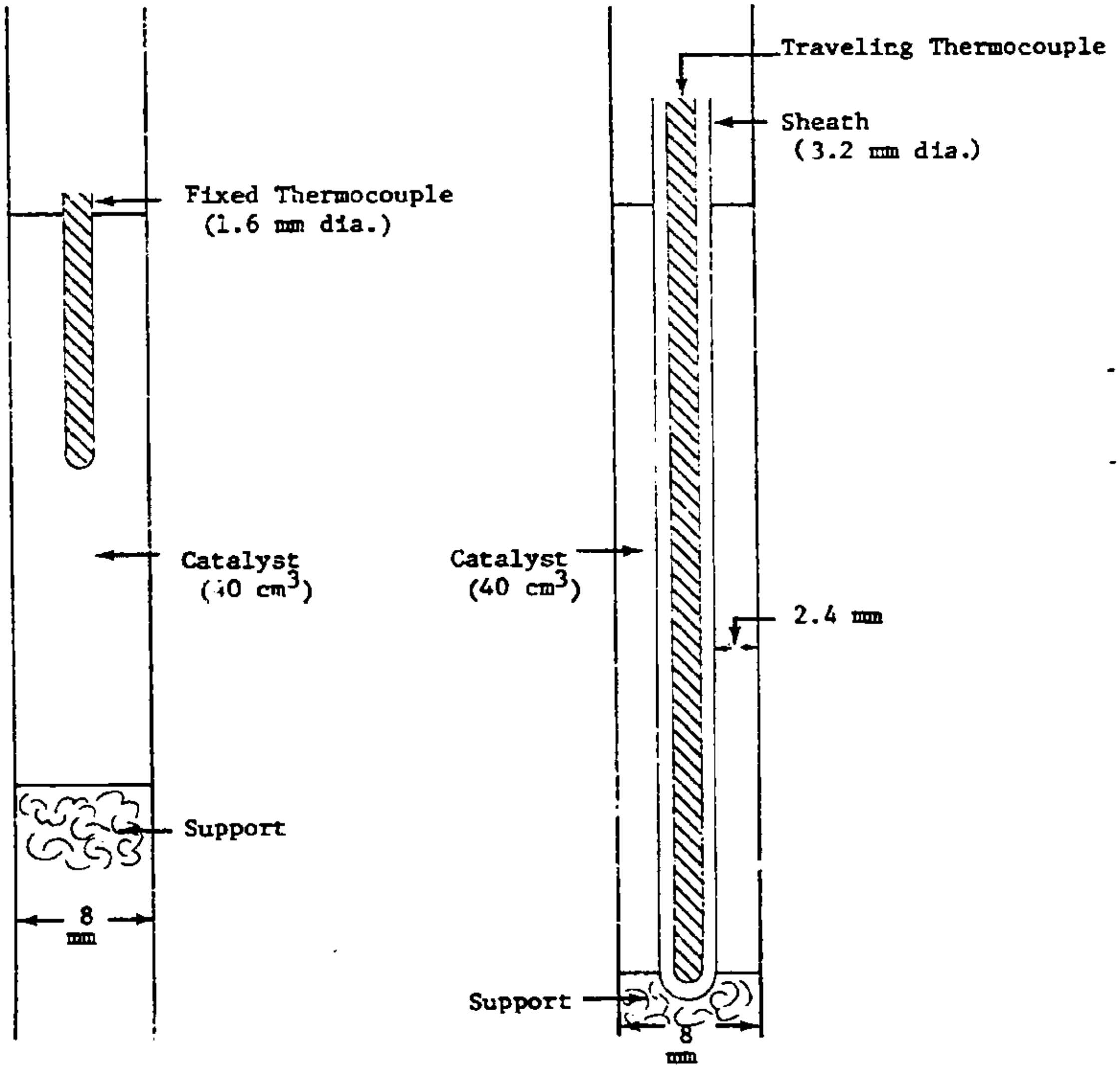
b. Larger amount of CO would be used to give C_5+ hydrocarbons in reactor B.

c. The selectivity to C_5+ hydrocarbons and the contraction would be higher in reactor B.

However, the results obtained from reactors 5 and 7 for run 4 have been shown in the section discussing reproducibility of results to be close. Similarly experimental values for reactors 5, 6, and 7 in run 5 (Appendix D) are also very close to one another. This identity of results in the two, differently packed reactor systems substantiates the premise that radial temperature gradients are not masking our results.

Figure 2.4

Thermocouple Placements in Run 5



Reactors 1 to 5, 7 (A)

Reactor 6 (B)

In order to further indicate the validity of the above arguments, we shall discuss an experiment in which temperature gradients were most probably present. Experiment 4-8 was performed at a high temperature, 215°C ± 3°C. This is an extreme temperature for the cobalt catalyst, and 98+% conversion of the reactants was obtained. Under such extreme conditions, a hot spot was noted about 5 cm from the top. The temperature of the spot was 318°C, and this was 100°C higher than anywhere else in the reactor. The hot spot was extremely small, and the temperature 1 cm below the spot was 220°C. The temperature of the hot spot decreased by more than 50°C during the course of the run. The temperature profile along the rest of the bed was flat. It was also noted in Experiment 4-8 that the results of reactors 5 and 6 were very similar to one another but were quite different from the results obtained from reactor 7 (Figure 2.3). Assuming that radial temperature gradients were now present at the high reaction temperature, then due to the reasons given above, reactor 7 would have a much smaller radial temperature gradient than reactors 5 and 6. The selectivities would be different as indicated above.

This is exactly what was found during Experiment 4-8 as shown in Table 2.5.

The above analyses of the possible interference of various aspects of transport phenomena indicate the complexities involved while studying the FT reaction. Catalyst particle sizes greater than about 0.02 cm would magnify problems associated with pore diffusion and perhaps also with internal heat transfer. However, the use of small particles reduces Re_p and hence k_m and h. And this reduction of the transfer coefficients, in turn, could lead to problems regarding external heat and mass transfer. This could probably be offset by using space-velocities higher than 300 V/V/h, but care would have to be taken to note whether increased space-velocities significantly changed the selectivity patterns of the reaction. Finally, the use of tubular reactors with internal diameters greater than about 0.8 cm and the use of short packed beds could lead to problems associated with radial and axial dispersion effects.

Table 2.5

Results from Reactors 5, 6, 7 in Experiment 4-8
Refer to Figure 2.3

Reactor	5	6	7
Nominal S, wt %	0	0	0
Pressure, kPa	1600.00	1600.00	1600.00
Space-velocity, V/V/h	215.00	213.00	218.00
Inlet H_2 flow, cm^3/min	120.06	118.72	121.43
Inlet CO flow, cm^3/min	59.39	58.72	60.05
Reactor temperature, °C	212.00	216.00	215.00
Avg. contraction, %	73.67	72.24	89.34
CO_2-free contraction, %	81.32	80.17	92.96
H_2 converted, cm^3/min	118.11	116.45	118.46
H_2 converted, µmol/min	4723.21	4656.52	4737.25
H_2 conversion, %	98.37	98.08	97.56
CO converted, cm^3/min	59.30	58.63	59.97
CO converted, µmol/min	2371.25	2344.50	2398.34
CO conversion, %	99.84	99.84	99.86
H_2 usage ratio	0.66	0.66	0.66
Gaseous products, µmol/min			
CH_4	1033.21	1076.95	281.79
C_2H_6	70.42	57.21	32.46
C_2H_4	0.00	0.00	0.00
C_3H_8	36.95	29.37	31.04
C_3H_6	0.00	0.00	0.00
n-C_4H_{10}	18.57	16.79	15.56
1-C_4H_8	0.00	0.00	0.00
CO_2	549.28	562.46	262.58
Total hydc. gas, µmol/min	1159.15	1180.32	360.86
CO converted to gas, µmol/min	1908.50	1909.12	764.70
CO conv. to hydc. gas, µmol/min	1359.21	1346.65	502.11
CO converted to C_5+ hydrocarbons			
µmol/min	462.75	435.38	1633.64
cm^3/min	11.57	10.88	40.85
Selectivity, % CO converted to:			
C_5+	19.51	18.57	68.11

It can be concluded that in Experiment 4-8 reactors 1 to 6, which have been packed in the usual way, have large radial temperature gradients, and correspondingly the production of condensed hydrocarbons is quite low.