

industrial applications. For example, a F-T derived hydrocarbon or oxygenate added to the feed gas might shift the product distribution from gasoline towards products in the diesel range.

Several studies were conducted in which ^{14}C -labeled ethylene was incorporated (1-6%, over iron catalyst) into higher hydrocarbons [Hall et al. (1960); Schulz et al. (1970)]. Most of the ethylene added was hydrogenated to ethane. Dwyer et al (1970), however, reported that ethylene addition shifted the selectivity to heavier products. In addition to reviewing the literature, Satterfield et al. (1983) performed experiments in a CSTR and found no change in product selectivity in the C_3 to C_8 range. Satterfield also concluded that Dwyer's findings probably resulted from experimental artifacts. Summerhayes (1982) established that 1-Butene added to the syngas feed was not significantly hydrogenated to butane. In addition, a study conducted at SASOL in which olefins were recycled to the fluidized bed reactor, no olefin incorporation was observed [Dry (1981)]. These two studies suggest that both paraffins and olefins are formed by primary reactions and that once olefin molecules larger than ethylene detach from the catalyst site they are not readsorbed.

Recently, attention has turned to the use of alcohols as possible feed additives [Huff (1983)]. Roofer-DePorter (1981) reports a possible F-T mechanism involving alcoholic intermediates. If alcohols produced in the F-T reaction desorb and readsorb onto different catalyst sites and further react to form higher products, then an alcohol added to the feed should cause a shift in the product distribution. Thus, methanol would be a good candidate for product incorporation studies.

2.3 Objectives and Method of Approach

The objectives of our study were (1) to determine the activity and selectivity of an iron-copper Fischer-Tropsch catalyst in a continuous stirred slurry reactor as a function of space velocity and H_2 to CO feed ratio and (2) to determine the extent to which methanol was incorporated into the Fischer-Tropsch reaction to form higher molecular weight products.

To meet the first objective, we determined catalyst activity by measuring CO and H_2 conversion over the range of operating conditions shown in Table (2-4). Selectivity was determined by analyzing product distributions for each set of experimental conditions.

Two measures of catalyst performance were used to evaluate the iron-copper Fischer-Tropsch catalyst used in this study. These were the CO conversion, x_{CO} , defined by

$$x_{\text{CO}} = 1 - \frac{\text{moles CO in effluent}}{\text{moles CO in feed}} \quad (2-9)$$

Table (2-4)
Range of Experimental Conditions for CSTR

Reactor Temperature	227°C
Reactor Pressure	790kPa.(100 psig)
Inlet Feed	2:1, 1:1, H ₂ :CO
Inlet Flowrate	0.3 - 1.0 liters/min.
Weight of Solvent	350 g
Weight of Unreduced Catalyst	84 g
Methanol Injection Flowrate	0 - 0.2 ml/min.

and the selectivity, represented by the Flory chain-growth probability, α (see Section 2.2.3). CO conversion is an easily measured indicator of catalyst activity, since the more active the catalyst, the higher the CO conversion at constant temperature and space velocity.

To meet the second objective we added methanol continuously to our reactor under conditions identical to a previous run with no methanol addition. By comparing the product distributions and CO conversions in the two runs we were able to assess the degree to which methanol was incorporated into the Fischer-Tropsch synthesis.

3 APPARATUS AND PROCEDURE

3.1 Slurry CSTR

A drawing of the one-liter Autoclave Engineers continuous stirred tank reactor used in this study is presented in Fig. (3-1). The reactor was equipped with a thermocouple port and a Dispersamax six-blade impeller mounted on a shaft driven by an Autoclave Engineers variable speed electric motor. The feed gas entered through a dip tube and was bubbled through a slurry consisting of 60 grams of fine (smaller than 53 mesh) Fe-Cu catalyst particles suspended in 350 grams of distilled octacosane. Octacosane ($C_{28}H_{58}$) was chosen as the solvent for the F-T slurry reactor since it will not compete with the F-T reactants to adsorb and react on the active sites of the catalyst and because of its low volatility [Huff (1982)]. Product gases and unreacted feed exited the reactor through a gas outlet port at the top of the reactor. Reactor temperature was maintained to within $1^{\circ}C$ with an electric heating mantle and an air cooling coil, each controlled separately.

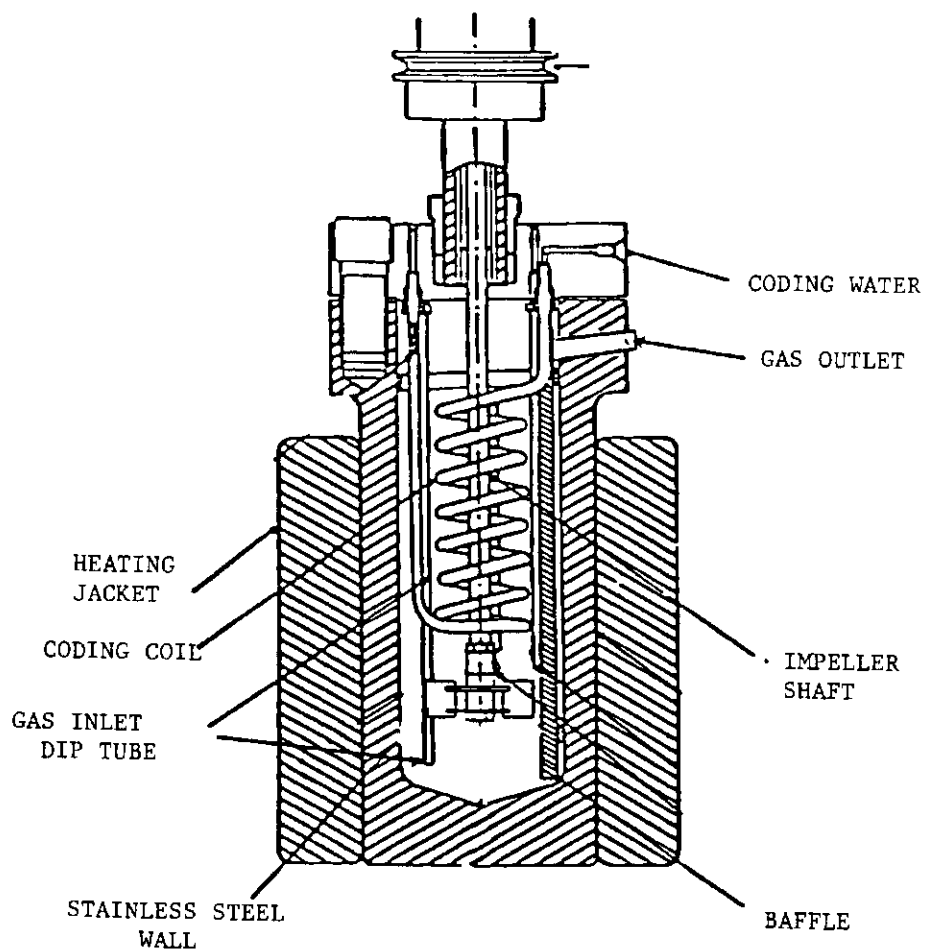
3.2 Feed and Product Handling

A schematic of the feed and product handling system is shown in Fig. (3-2). Feed gas (Argon, pre-mixed 2:1 or 1:1 H_2 to CO synthesis gas, or hydrogen) entered the system through a gas manifold and the inlet pressure was set by a pressure regulator. The flow rate was regulated by a differential pressure cell and a control valve which were made insensitive to downstream pressure changes by a back-pressure regulator set at 150 psig and located immediately upstream of the reactor. Feed gas was either bubbled through the reactor or sent directly to the on-line gas chromatographs (GC's) and soap-bubble flowmeters. Higher molecular weight products from the reactor were collected in two traps, one at $60^{\circ}C$ and the other at $0^{\circ}C$. Pressure in the reactor was maintained by means of a back-pressure regulator set at 100 psig and located downstream of the $60^{\circ}C$ trap. The effluent gas from the traps was analyzed using gas chromatography and the flow rate was measured with the soap-bubble flowmeter.

3.3 Preparation and Reduction of the Iron-Copper Catalyst

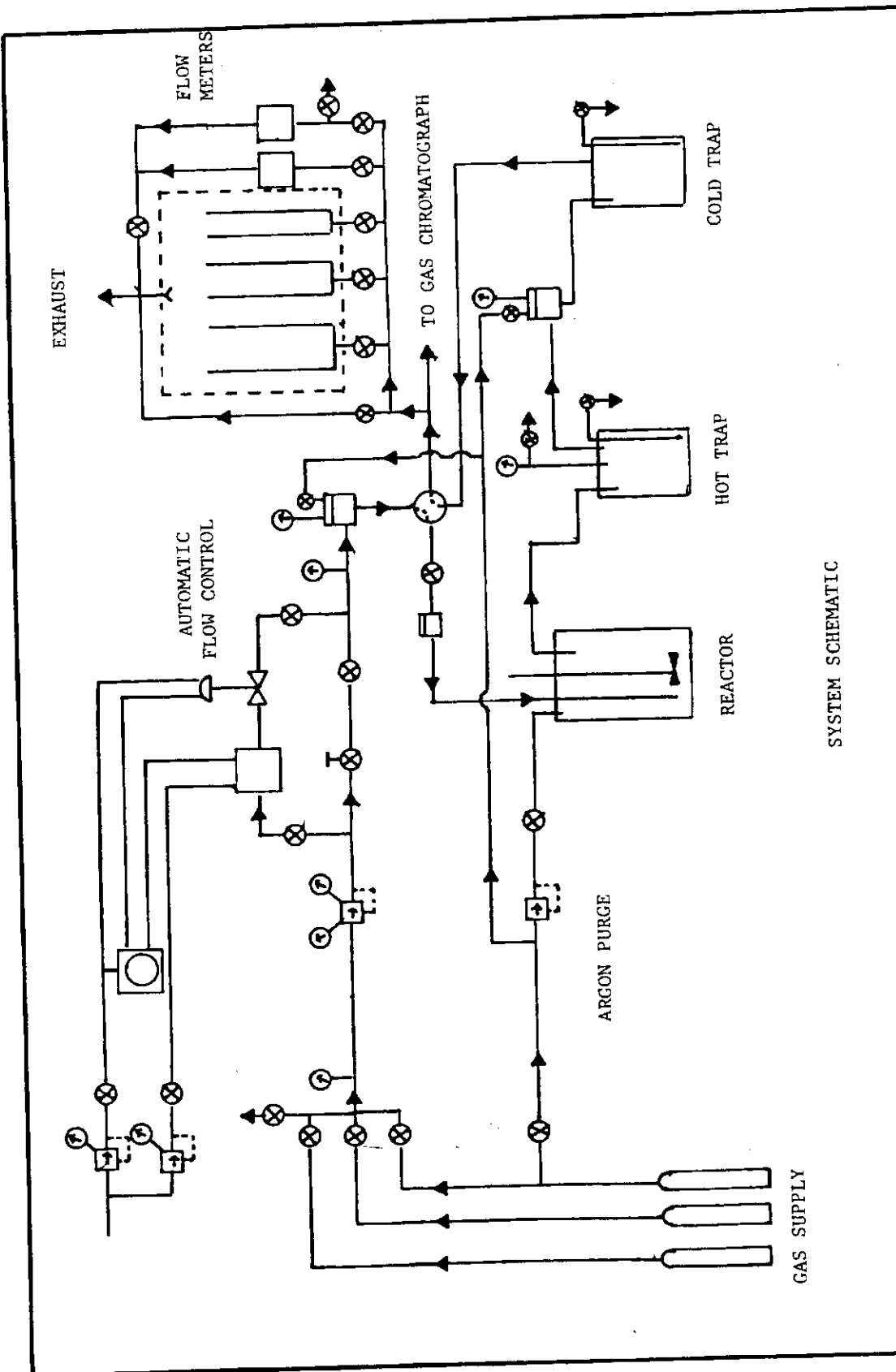
The iron-copper catalyst used in this study was prepared as follows. A ferric nitrate-copper nitrate solution was made by dissolving 288 g of ferric nitrate and 46 g of copper nitrate in one liter of boiling water. The iron and copper in the solution were then coprecipitated by the addition of a hot solution of 160 g of sodium carbonate dissolved in 1.5 liters of water. The precipitate, having the consistency of a gel, was filtered and placed in a crystallizing dish. This gel was then impregnated with 0.2 g of potassium carbonate dissolved in 160 ml of hot water and hand stirred until the gel was very thick. The iron-copper gel was then dried in an oven at $105^{\circ}C$ for 24 hours. Upon removal from the oven, the catalyst was cooled in air, crushed, screened to a size less than 53 mesh, and stored in air.

REACTOR DRAWING



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DATE 8-4-83	DRAWN BY BRS	FILE NO MIT BNL 83-4	FIG 3.1
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SYSTEM SCHEMATIC

MASSACHUSETTS INSTITUTE OF TECHNOLOGY SCHOOL OF CHEMICAL ENGINEERING PRACTICE	DATE 8-4-83	DRAWN BY BRS	FILE NO MIT BNL 83-4	FIG 3.2
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Just prior to use, 84 grams of catalyst was placed in a horizontal glass tube fitted with valves at both ends. The tube was slowly heated to 270°C under hydrogen flow to reduce the catalyst. To complete the reduction the catalyst was maintained at 270°C for four hours. Finally, the catalyst was brought slowly down to room temperature and used immediately.

3.4 Catalyst Loading

The pyrophoric nature of the reduced iron-copper catalyst required charging the catalyst into the reactor under an inert argon atmosphere. Before loading, the reactor was brought to a temperature of 100°C to melt the octacosane solvent. Then, the catalyst was poured from the glass tube in which it was reduced (see Section 3.3) into the top of the reactor under a flow of argon gas. At the same time, argon gas was both passed over and bubbled through the reactor to insure that the catalyst was not exposed to oxygen. After the reactor was sealed and pressurized to 100 psig, it was brought up to the reaction temperature of 227°C under an H₂ atmosphere. At this time synthesis gas was introduced into the reactor. Steady-state catalyst activity was attained after 16 hours of exposure to synthesis gas.

3.5 Solvent Preparation

The liquid solvent, octacosane (C₂₈H₅₈) was obtained from the Humphrey Chemical Company. Before loading the octacosane into the reactor, it was vacuum-distilled at 210°C and 200 mm Hg to remove sodium bromide impurities. These impurities resulted from the Wurtz reaction, which is used to synthesize octacosane [Morrison and Boyd (1968)]. When the catalyst lost activity and the reactor was shut down, the octacosane solvent containing spent catalyst was reprocessed. The old catalyst was removed by hot filtration. Oxygenated hydrocarbon impurities formed in the reactor were then removed by extraction with tetrahydrofuran. As a final purification step, the octacosane was distilled at 205°C and 100 mm Hg.

3.6 Product Analysis

Fischer-Tropsch products were analyzed qualitatively by nuclear magnetic resonance, and quantitatively by gas chromatography. Three gas chromatographs (GC's) were used to analyze the product gases exiting the system. Hydrogen was analyzed on an on-line Carle GC with a molecular sieve column at room temperature and a thermal conductivity (TC) detector. This GC broke down during runs 3 and 5, so H₂ concentrations for these runs were estimated as shown in Section 8.3. Carbon monoxide, carbon dioxide, and methane were analyzed on another on-line Carle GC with a Porapak Q column at 80°C, and a TC detector. Other gaseous products were analyzed by injecting 50µl of the gas into an off-line Carle 211 GC with a Chromosorb 102 column at 140°C and a flame ionization detector (FID).

Three other gas chromatographs were used to analyze the liquid samples: a Hewlett-Packard 5730A, a Perkin-Elmer 900, and a Gow-Mac 750. Aqueous

samples were chromatographed on a chromosorb-102 column, temperature programmed from 60 to 250°C at a rate of 8°C/min., in the HP-5730A GC with a TC detector. The organic phases from both the hot and cold traps were mixed together and chromatographed on an SE-30 column, temperature programmed from 80 to 300°C at a rate of 8°C/min., in the PE-900 GC with an FID detector. These two GC's showed carbon number distribution, but could not resolve paraffins from olefins. Paraffins and olefins with 9 or more carbon atoms were resolved on a capillary column, temperature programmed from 80 to 250°C at a rate of 8°C/min., in a Gow-Mac 750 GC with an FID detector. A summary of analysis techniques is presented in Table 3.1.

Table (3-1)
Summary of Analysis Techniques

Species	Device	Column	Temperature	Detector ¹	Accuracy
H ₂	On-line Carle	Molecular Sieve	Room Temp.	TC	10%
CO	On-line Carle	Parapak Q	80°C	TC	10%
CO ₂	On-line Carle	Parapak Q	80°C	TC	10%
H ₂ O	No Analysis	---	---	---	---
CH ₄	On-line Carle	Parapak Q	80°C	TC	10%
C ₂ - C ₇ Aliphatic	Carle 211	Chromosorb 102	140°C	FID	15%
CH ₃ OH	Carle 211	Chromosorb 102	140°C	FID	15%
C ₂ - C ₅ Alcohol	HP	Chromosorb 102	60-250°C	TC	10%
C ₆ + Alcohols	HP	Chromosorb 102	60-250°C	TC	10%
C ₈ - C ₂₈	No Analysis	---	---	---	---
C ₉ - C ₁₉	P-E	SE-30	80-300°C	FID	20%
Paraffin to Olefin Ratio	Gow-Mac	Capillary	80-300°C	FID	20%

¹TC = Thermal Conductivity Detector
FID = Flame Ionization Detector

For each peak in a GC trace, the area under the response curve corresponds to the amount of material present. In these experiments, areas were computed using Hewlett-Packard 3090 or 3088 programmable integrators. The amounts of hydrogen, carbon monoxide, carbon dioxide, and methane were determined by filling the sample loop of the GC with pure gas standards and noting the area of the peak. Reaction products were then introduced into the same sample loop, and the mole fraction of each compound was found by dividing the area of each peak by the area of the standard peak. Linearity of detector response was confirmed by introducing the feed gas into the sample loop and making sure that the correct H₂ and CO concentrations were obtained. Olefin fractions for C₉ and above were determined by dividing the area of the olefin peak by the sum of the olefin and paraffin peaks.

Since methane was visible on the Carle 211 off-line GC (H₂, CO, and CO₂ are not detected by FID detectors) as well as the on-line GC, it was used as a reference for all other peaks on the Carle 211. After GC peaks were identified, areas were divided by the appropriate sensitivity factors [McNair and Bonelli (1968)] and renormalized to obtain weight percent. From a knowledge of the total amount of methane, the total amounts of other compounds could then be calculated. Quantitative determinations of liquid-phase products were made by multiplying peak areas by appropriate response factors, renormalizing to get weight percent and multiplying by the total sample weight to obtain the total weight of each product.

3.7 Experimental Errors

3.7.1 Sampling Technique. The slurry reactor used in this study is continuous with respect to the gas phase but batch with respect to both the liquid and solid phases; all of the reaction products leave the reactor in gaseous form. Thus, for the amount of a particular product in the reactor effluent to be equal to the amount of that product produced by reaction, vapor-liquid equilibrium must be attained in the reactor, otherwise product accumulation will occur. After each catalyst loading, however, the reactor contained only pure octacosane, and thus there was a time delay during which the higher molecular weight products accumulated in the reactor.

Huff (1982) calculated the time necessary for heavy products to appear in the gas phase at 263°C, 790 kPa, and a space velocity of 2320 hr⁻¹. Huff's results are presented in Fig. (3-1), where time is plotted on a log scale as a function of carbon number. After 1 hour, for example, approximately 85% of C₆, 70% of C₈, 45% of C₁₀, and 30% of the C₁₂ produced by the F-T reaction are present in the reactor effluent. These results suggest that after the initial start-up time of 18 hours, representative samples for C₁₁ and lower were obtained. Measurements for the higher molecular weight products are expected to be low, but since the mole fraction of product decreases exponentially with increasing carbon number (see Section 2.2.3, Product Selectivity), this error should not significantly affect the total mass of products and the mole fraction of the light components.

Since no time was allowed for equilibrium to be reached between runs (except for the first run after a catalyst loading), significant errors in

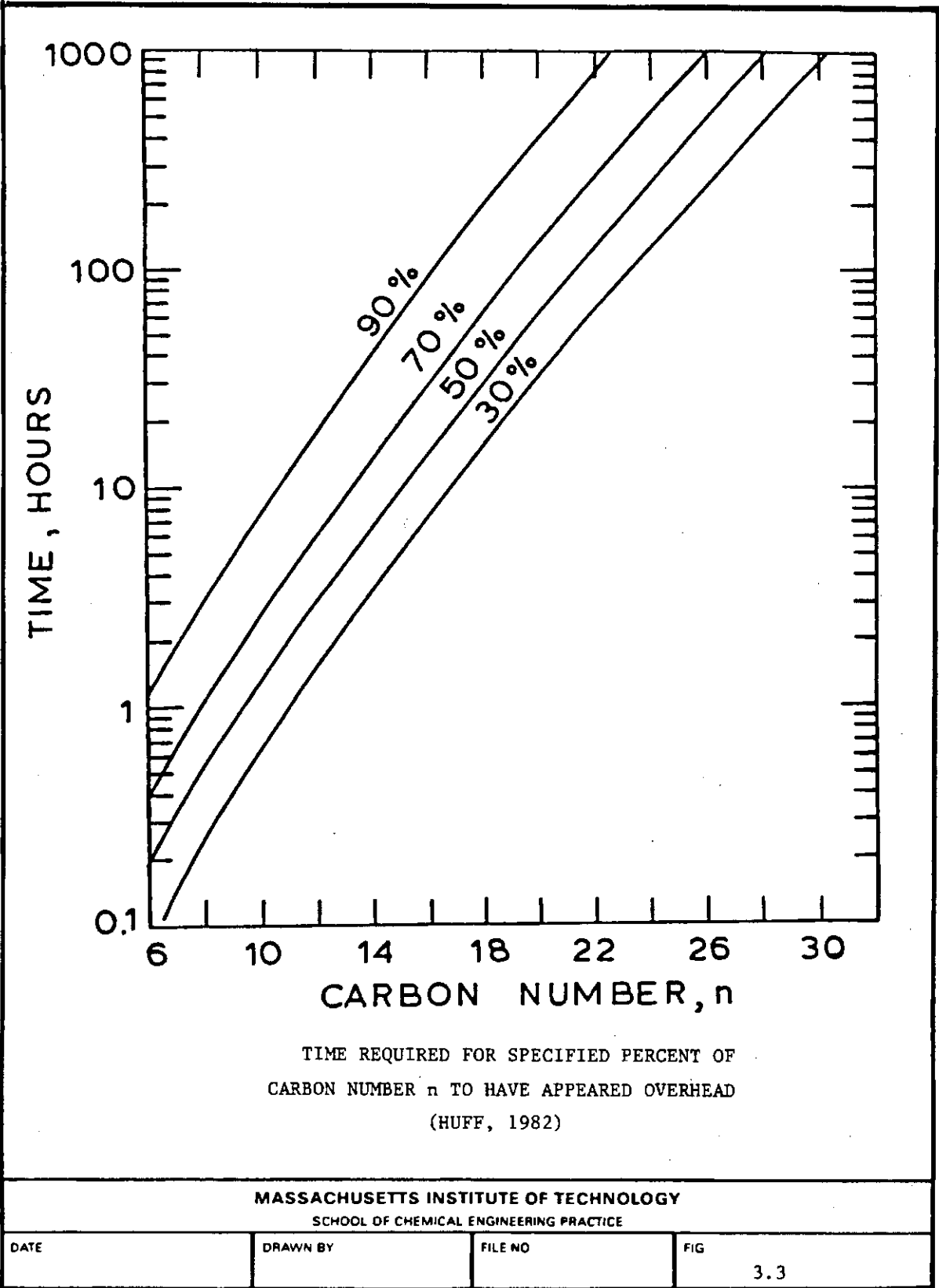
the C₆ and higher hydrocarbon range could occur if the product distribution changed dramatically between runs. These errors would be small, however, if the product distributions were similar, as they were for our experiments (see Section 4.6.1). Thus, we have the most confidence in our measurements of light hydrocarbons (C₁ - C₅) and the least confidence in our measurements of heavy hydrocarbons (>C₁₁).

Another intrinsic source of error in the measurement of the higher molecular weight products was introduced by the design of the liquid traps. The 60°C trap was upstream of the 100 psi back-pressure regulator, and therefore some products could have been lost due to flash evaporation (caused by the sudden change in pressure) when the trap was opened. Also, both traps had a volume of 300 ml, but when samples were collected after each 12 hour run, only 5 to 10 ml of liquid were in the traps. Because of the large size of the traps, small quantities of products could have been lost on the trap walls.

3.7.2 Gas Chromatography. A major flaw in the analysis of the F-T products was that the Carle 211 GC could not detect water in the gas effluent from the 0°C trap. From an oxygen balance and a calculation of vapor-liquid equilibrium in the 0°C trap we estimated that at least 50% of the water produced in the reactor did not condense in the trap and was not detected by the GC. The Carle 211 GC also could not detect hydrocarbons higher than heptane, so any uncondensed higher molecular weight hydrocarbons were not detected. Also, there was no resolution of paraffins, olefins, isomers, or higher alcohols in the gaseous effluent.

The aqueous liquid samples contained only water and alcohols, so analysis was fairly simple, and the HP-5730A was able to resolve the components well. The organic liquid samples were more complex, however, and the Perkin-Elmer 900 could not resolve alcohols, paraffins, olefins, or isomers of any of the above. Another difficulty was that the carbon number of the alcohol in a peak was three less than the carbon number of the paraffin and olefins. For example, hexanol came out with nonane and nonene. This was a problem for two reasons. First, peaks did not represent only one carbon number. Second, alcohols have different response factors than do olefins and paraffins, and therefore quantifying the results was difficult. Fortunately, the alcohols constituted only about 10% of the product, so the errors in the analysis of the heavier hydrocarbons should be within 10% also.

3.7.3 Peak Integration. The Hewlett-Packard 3090 and 3088 integrators used in this study are very accurate when peaks are well defined, but when peaks are merged or have shoulders, the integrators cannot distinguish where one peak ends and another begins. This problem arises in the case of poor resolution of isomers on the GC, especially for the low and high molecular weight ranges (C₂ and C₆ and above for the Carle 211 and C₅ - C₉ and C₁₉ and above for the Hewlett-Packard and the Perkin-Elmer). Thus, when peaks were not well resolved, or had shoulders, the group of peaks was combined and an average response factor was used.



4 RESULTS AND DISCUSSION

4.1 Outline of Experiments Performed

In this study seven experiments, each 12 hours in duration, were conducted in a slurry CSTR using an iron-copper catalyst. A summary of the experimental conditions is presented in Table (4-1). In the first three experiments the effect of space velocity on the activity and selectivity of the catalyst was studied. After the third run, experimental problems resulted in catalyst deactivation, and a new batch of catalyst was charged to the reactor. The fourth experiment was conducted with this new catalyst charge under conditions similar to those of the second experiment to determine if the activity and selectivity could be reproduced. In run 5 we investigated the effect of the H₂ to CO feed ratio on catalyst activity and selectivity by changing this ratio from 2:1 to 1:1. Run 6 was conducted as a reproducibility check to determine if catalyst performance was affected by the 1:1 H₂ to CO feed in run 5. Finally, methanol was added continuously to the reactor along with the syngas feed to determine whether methanol could be incorporated into the Fischer-Tropsch reaction.

Table (4-1)
Experimental Conditions

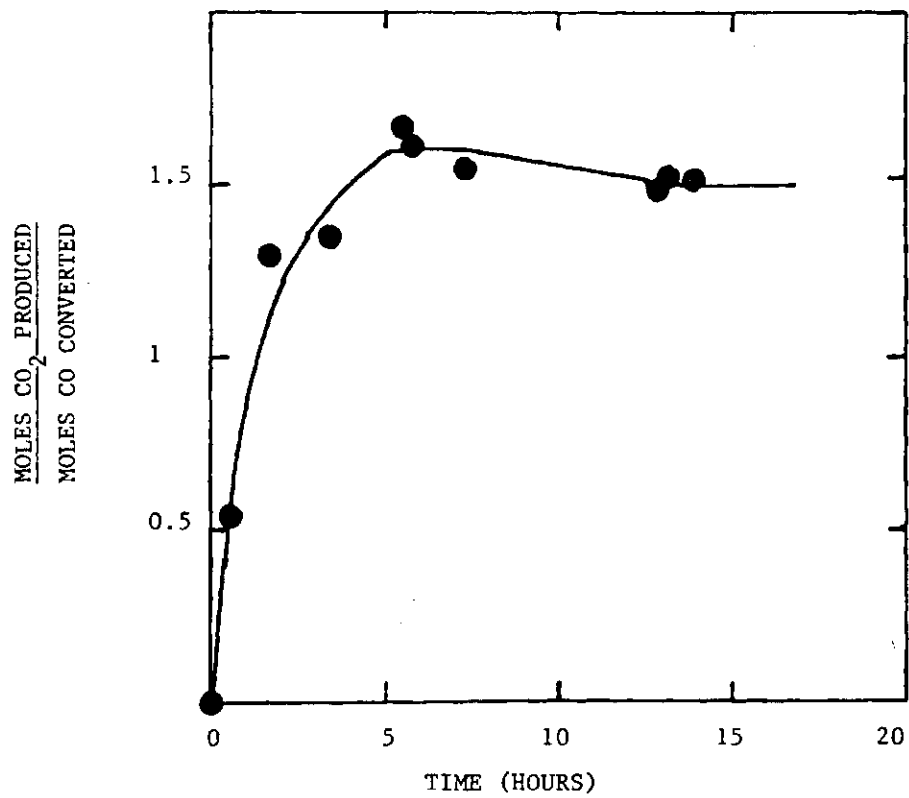
Run No.	Pressure psig	Temperature °C	Space Velocity hr ⁻¹	Syngas Ratio H ₂ :CO	Catalyst Batch
1	100	227	1572	2:1	1
2	100	227	953	2:1	1
3	100	227	488	2:1	1
4	100	227	923	2:1	2
5	100	227	828	1:1	2
6	100	227	935	2:1	2
7*	100	227	935	2:1	2

*Methanol Incorporation.

4.2 Steady State Catalyst Activity

After a new batch of catalyst was added to the reactor, the activity rapidly increased to a high initial value before slowly declining to a steady-state level. This is shown in Fig. (4-1), where CO₂ production normalized against unreacted CO in the effluent is plotted as a function of time for the second catalyst campaign. A maximum CO₂ production of 1.65 moles CO₂/mole of unreacted CO was observed approximately seven hours after the initial exposure of the catalyst to syngas, as compared to the steady-state value of 1.49 moles CO₂/mole unreacted CO which occurred 12-15 hours after start-up. This decrease in activity was attributed to carbon deposition of the most active catalyst sites by the Boudouard reaction, Eq. (2-3). Since the Boudouard reaction consumes CO and produces CO₂, a maximum in CO₂ production would be expected during the initial period of catalyst

MOLES CO₂ PRODUCED
MOLES CO CONVERSION VS TIME (HOURS)
FOR STEADY STATE ACTIVATION



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FIG
4.1

activity. The time required for catalyst to attain steady-state was similar to that reported by Huff (1982) who found that steady-state was achieved 12-20 hours after loading for an iron-ammonia synthesis catalyst.

4.3 Mass Transfer Considerations

An experiment was conducted in which the stirring speed was reduced from 650 to 500 rpm for about 2 hours. No decrease in CO conversion was observed after this change was made. If mass transfer limitations were present, a drop in conversion would have occurred when the stirring speed was reduced. Thus, mass transfer limitations did not exist at either 500 or 650 rpm. All other experiments were run with a stirring speed of 650 rpm.

4.4 Effect of Space Velocity

4.4.1 CO Conversion. The carbon monoxide conversion is plotted as a function of space velocity for each of six experimental runs in Fig. (4-2). CO conversion increased with decreasing space velocity from 58% at 1572 hr⁻¹ to 92% at 488 hr⁻¹. In addition, Fig. (4-2) shows a reproducibility point (point 4) comparing the second batch of catalyst with the first batch. As shown in this figure, the performance of the two catalyst batches was indistinguishable.

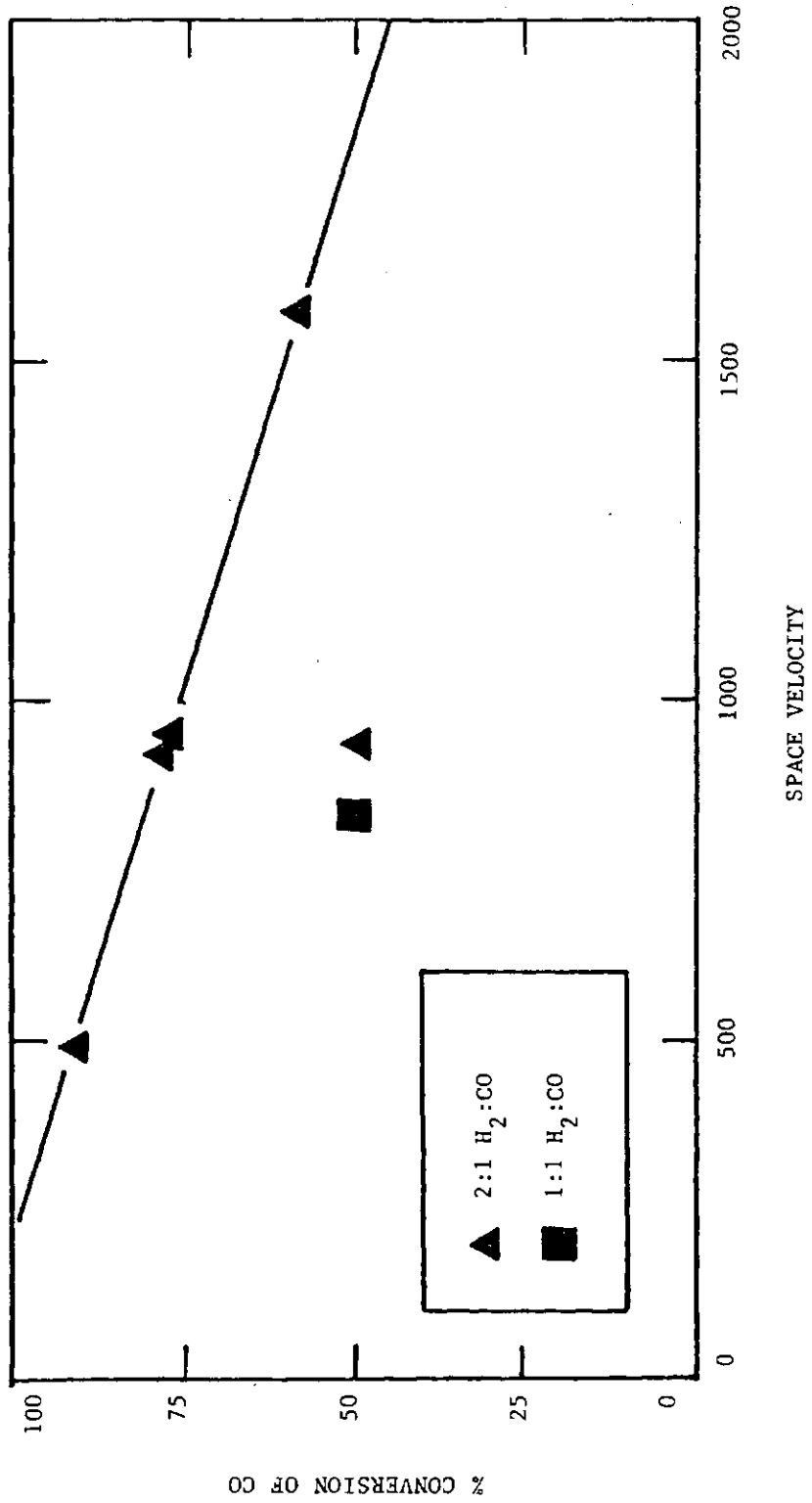
The observed trend of increasing CO conversion with decreasing space velocity for runs 1 to 4 was due to an increase in the average residence time of the CO and H₂ in the reactor. As residence time increased, the probability of a CO molecule adsorbing on the catalyst surface and reacting increased, resulting in higher conversions of CO.

Carbon monoxide conversions obtained in this study are compared to values reported in the literature for similar reaction conditions in Table (4-2). The CO conversions reported by Huff (1982) with an iron-ammonia synthesis catalyst were about 30% higher than those we obtained with our iron-copper catalyst at similar temperatures and space velocities. The conversions obtained by Schlesinger et al. (1951) were similar to ours, but were obtained at higher temperatures.

Table (4-2)
Conversions of CO and CO + H₂ in Various Studies Using Iron Catalysts

Author	Temperature (°C)	Pressure (KPa)	H ₂ /CO	Space Velocity (hr ⁻¹)	% Conversion	
					CO	CO + H ₂
Present work	227	790	2:1	1572	58	33
Huff (1982)	232	790	1.81:1	1520	80	48
Huff (1982)	232	790	0.9:1	1460	65	55
Schlesinger et al. (1951)	238	790	1:1	1000	21	24
Schlesinger et al. (1951)	255	790	1:1	875	55	43
Present work	227	790	1:1	828	50	41

EFFECT OF SPACE VELOCITY ON CO CONVERSION



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FIG.
4.2

4.4.2 H₂ + CO Conversion: Decoupling the F-T and the Water-Gas Shift Reactions. Carbon monoxide conversion is a measure of catalyst activity for the combined Fischer-Tropsch and water-gas shift reactions, as they both consume this reactant. A common method of decoupling these reactions and examining the activity of the catalyst with respect to the F-T reaction alone is to measure the H₂ + CO conversion, X_{H₂ + CO}, defined as

$$X_{H_2 + CO} = \frac{(\text{moles of CO consumed}) + (\text{moles of H}_2 \text{ consumed})}{\text{moles of H}_2 + \text{CO fed}} \quad (4-1)$$

By measuring the H₂ + CO conversion, the effect of the water-gas shift reaction is negated because one mole of H₂ is formed for each mole of CO consumed:



Thus H₂ + CO conversion for the water-gas shift reaction is zero.

Conversion of CO + H₂ is plotted versus space velocity for six runs in Fig. (4-3), and, like CO conversion, increases with decreasing space velocity. This is due to an increase in the residence time of CO and H₂ in the reactor, as explained in Section 4.4.1.

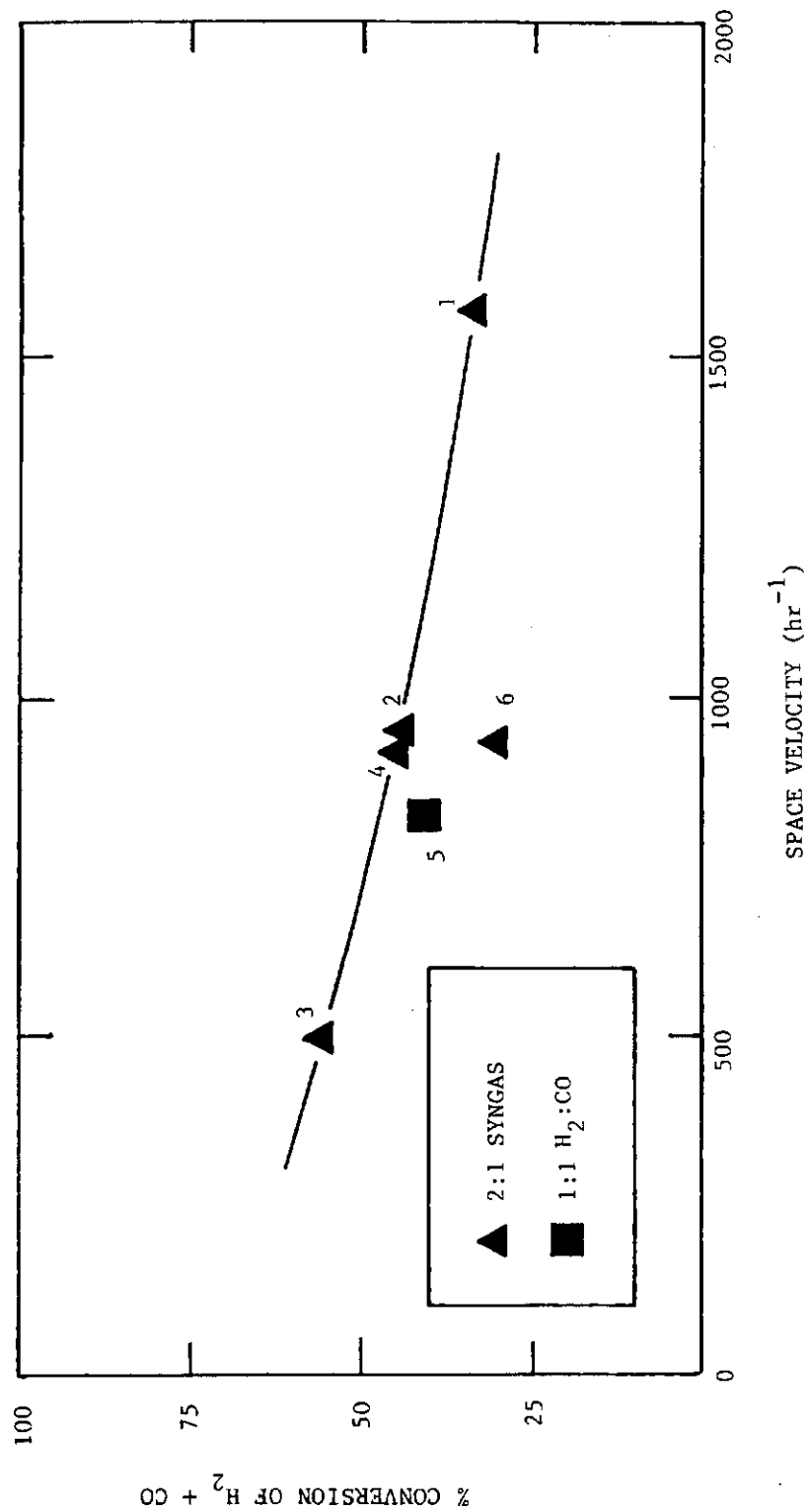
In Table (4-2) we also compare the H₂ + CO conversions obtained in this study with those obtained by Huff (1982) and Schlesinger et al. (1956) for similar space velocities. The results of this comparison were similar to those obtained for CO conversion, with Huff's iron-ammonia catalyst exhibiting a higher activity than the iron-copper catalyst used in this study and Schlesinger's catalyst attaining H₂ + CO conversions similar to ours, but at significantly higher temperatures.

4.5 Effect of H₂ to CO Feed Ratio

In experiment 5 the ratio of H₂ to CO in the synthesis gas feed was reduced from 2:1 to 1:1. After steady-state was achieved (12 hours) the measured CO conversion (Fig. (4-2)) was 50% at a space velocity of 828 hr⁻¹, a decrease from the 77% observed at 923 hr⁻¹ using 2:1 synthesis gas (run 4). The H₂ + CO conversion (Fig. (4-3)) decreased from 44.5% to 41.0%, and the extent of the Fischer-Tropsch reaction, f, defined as the moles of CO participating in the F-T reaction per mole of CO fed (see Section 4.7, Eq. (4-9)), decreased 39% from 0.422 to 0.259.

These decreases were expected, for, as shown in Section 2.2.2, the simplified rate expression for F-T synthesis proposed by Anderson (1956) is first order with respect to hydrogen partial pressure and zero order with respect to CO partial pressure (in the absence of mass transfer limitations). Table (4-3) lists the partial pressures of hydrogen in the reactor for runs 1-6 (see Appendix 8.2.2).

EFFECT OF SPACE VELOCITY ON CO + H₂ CONVERSION



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FIG. 4.3

Table (4-3)
Partial Pressure of Hydrogen in the Reactor
Runs 1-6

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
P_{H_2} kPa	520	529	496	524	362	513
P_{H_2} psig	66	67	63	67	46	65

For run 5, P_{H_2} was 362 kPa, 69% of the value of 524 kPa used in run 4. Using Anderson's rough kinetic model, the rate of Fischer-Tropsch reaction, r_{FT} , is given by:

$$r_{FT} = \frac{d[-CH_2-]}{dt} = k' P_{H_2} \quad (2-5)$$

This rate can also be expressed as:

$$r_{FT} = \frac{f}{1 + F} (SV) \frac{P_s}{R T_s} \frac{V_c}{V_R} \quad (4-2)$$

where

- f = moles CO participating in the F-T reaction per mole CO fed
- F = feed ratio, moles H_2 fed per mole CO fed
- (SV) = space velocity, volume of feed gas at STP per volume of catalyst
- P_s = standard pressure
- T_s = standard temperature
- R = ideal gas constant
- V_c = volume of catalyst
- V_R = volume of reactor

The last two terms in Eq. (4-2) were constant for all of our experiments. If we also assume a constant space velocity, this equation becomes

$$r_{FT} = K_R \frac{f}{1 + F} \quad (4-3)$$

where

$$K_R = \text{Constant} = (SV) \frac{P_s}{R T_s} \frac{V_c}{V_R} \quad (4-4)$$

Rearrangement of Eqs. (2-5) and (4-3) yields

$$f_1 = f_2 \frac{(P_{H_2})_1}{(P_{H_2})_2} \frac{1 + F_1}{1 + F_2} \quad (4-5)$$

where the subscripts 1 and 2 denote two experimental runs at the same space velocity but different H₂ to CO feed ratios.

Using Eq. (4-5), the expected value for f in run 5 is 0.194, 25% less than the experimental value of 0.259. Approximately 60% of this difference is because run 5 was at a space velocity of 828 hr⁻¹ while run 5 was at 923 hr⁻¹. The important feature in this analysis, however, is that the observed f is higher than the predicted value, indicating that the 1:1 H₂ to CO ratio did not adversely affect the activity of the catalyst.

This result could not be confirmed, however. Following the 1:1 H₂ to CO experiment the feed gas ratio was switched back to 2:1 at a space velocity of 935 hr⁻¹ and the observed carbon monoxide conversion was only 49%, compared to 77% at 953 hr⁻¹ and 78% at 923 hr⁻¹ for runs 2 and 4, respectively. In addition, H₂ + CO conversion was 30.6% and f was 0.290, compared with 44.4% and 0.421 (run 2), and 44.5% and 0.422 (run 4). These results indicate that a significant loss of catalyst activity occurred.

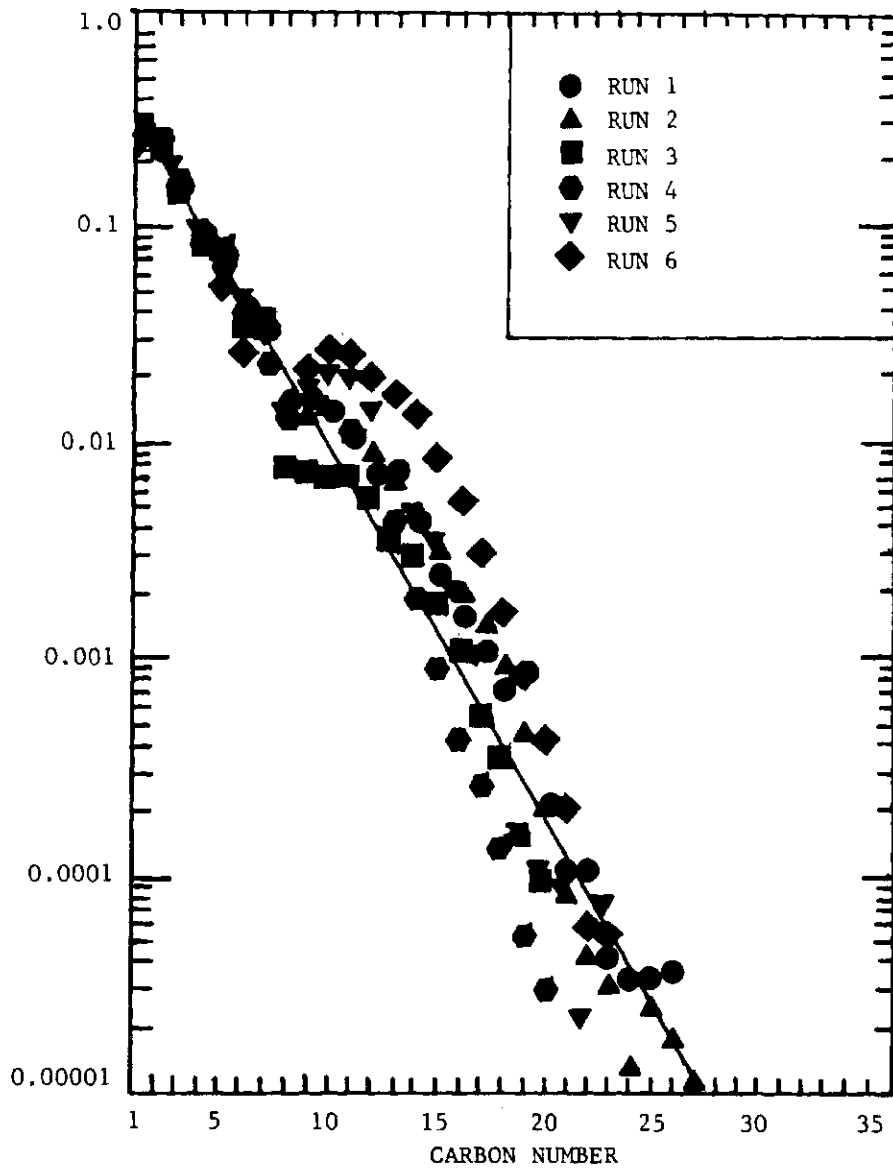
Because our analysis showed that the observed activity in run 5 was higher than the estimated expected activity, we postulated that the deactivation occurred during the changeover from 1:1 to 2:1 syngas. This would have been the case, for instance, if the lines leading into the gas intake manifold were not purged sufficiently, permitting the oxygen to enter the reactor and to oxidize and deactivate the catalyst.

There is, however, a more reasonable explanation. When the change from 2:1 to 1:1 syngas was made (between runs 4 and 5), the ratio of H₂ to CO partial pressures was roughly 7:1 (Appendix 8). But, when the feed was changed back to 2:1 syngas after run 5, the H₂ to CO partial pressure ratio in the reactor was only about 1:1. During the time interval in which the new syngas feed rate was being adjusted (about 10 minutes), there was no flow through the reactor, and the partial pressure of hydrogen would have dropped considerably as hydrogen was being consumed. As the hydrogen partial pressure dropped, conditions would become much more favorable for oxidation of the catalyst to occur, resulting in deactivation.

4.6 Product Analysis

4.6.1 Carbon Number Distribution. The organic products obtained in this study fit the Flory distribution described in Section 2.2.3. This is illustrated by the straight line shown in Fig. (4-4), in which the mole fractions of the product hydrocarbons are plotted on a log scale as a function of carbon number. The value of the chain growth probability, α , was calculated for carbon numbers 1 to 7, since the most accurate mole fraction determinations were made in this range (see Section 3.7), and a value of 0.67 ± 0.02 was obtained. This value is in the gasoline range and

CARBON NUMBER DISTRIBUTION
 AT 227° AND 790 KPa (100 PSI)



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is similar to values presented in the literature (see Table (2-3)). Huff (1982) reported α 's ranging from 0.67 to 0.71 for a fused-iron (ammonia synthesis) catalyst in a slurry CSTR at higher temperatures (232-268°C). Kölbel et al. used a catalyst very similar to ours and reported higher α 's (0.84-0.85) at higher temperatures (267°C), higher pressures (1.1-1.2 MPa, 162-176 psig) and higher space velocities (2500-3125 hr⁻¹) in a bubble column reactor. In addition, we observed no change in α when the space velocity was tripled (488 to 1570 hr⁻¹) or when the H₂ to CO feed ratio was changed from 2:1 to 1:1. These observations agree with the findings of Satterfield and Huff (1982).

As described in Section 3.7, a significant fraction of the high molecular weight products remain in the liquid phase of the reactor due to their low volatility. Since our product distribution data were taken before vapor-liquid equilibrium was reached (run times between 20 and 50 hours), the negative deviations from the Flory model at high carbon numbers shown in Fig. (4-4) were expected.

4.6.2 Paraffin-Olefin Selectivity. The olefin fractions, defined as the moles of olefins divided by the moles of olefins plus paraffins, is plotted as a function of carbon number in Fig. (4-5). Due to equipment limitations, the olefin fractions for carbon numbers 2 to 9 were not obtained. More olefins than paraffins were produced up to a carbon number of 14, while at higher carbon numbers the olefin fraction decreased as the selectivity shifted to paraffins, this trend being consistent with other reported studies [Huff (1982)]. This shift in selectivity may result either from the paraffins being more thermodynamically stable at higher carbon numbers, or from the olefinic nature of the products being a function of residence time on the catalyst surface, which increases with increasing chain length.

As shown in Fig. (4-5), when the space velocity was tripled (from 488 to 1572 hr⁻¹) the olefin fraction appeared to increase slightly (for C₉ the observed increase was 17%). Because the experimental error was of the same order as the observed increase, no definite conclusions could be reached. In addition, no reports of a trend linking olefin fraction to space velocity were found in the literature.

4.6.3 Average Fischer-Tropsch Reaction Product. The average organic product in Fischer-Tropsch synthesis can be approximated by C_n H_{2n+1}, and is calculated from the following equation derived by Huff (1982):

$$n = \frac{1}{1 - \alpha} - \frac{1}{14} \quad (4-6)$$

Since α was virtually constant for all our runs, the average value of 0.67 was used to obtain $n \approx 3$. Thus our average organic product was C₃H₇. The hydrogen to carbon ratio of 2.33 is identical to the value reported by Huff (1982) for his fused-iron catalyst.