potassium promoted version of the iron/kieselguhr catalyst was not tested.

All catalyst testing was performed at fixed temperature, pressure, flowrate, feed composition, and reactor loading. A standard simulated pyrolysis gas feed composition of 26 mole % hydrogen, 32 % carbon monoxide, 16 % carbon dioxide, 13 % methane, and 13 % ethylene was used. This composition is similar to the simulated pyrolysis gas feeds of previous catalyst testing performed at ASU. The remaining conditions were chosen with reference to other pilot-plant scale slurry phase Fischer-Tropsch studies which used precipitated iron catalysts.

High reaction temperatures leads to carbon formation and increases the selectivity towards lighter hydrocarbons, primarily methane. High temperatures in slurry reactors may also increase the rate of slurry liquid cracking (26). Kolbel (28) operated in the 216 - 270°C range when liquid fuels were the desired product. The lower portion of the range favored hard waxes while the upper favored products boiling in the gasoline range. The Rheinpreussen demonstration plant, intended to produce gasoline boiling range products, was operated at 268°C (21). Slurry reactor studies at the British

Fuel Research Station were conducted at 260°C, (21). In order to maintain a constant gas conversion over long periods, the temperatures were allowed to increase to a maximum of 280°C. Temperatures in the range of 240 - 270°C appear to be the most common for precipitated iron catalysts, so 260°C was selected as the most suitable temperature for catalyst testing.

Since the Fischer-Tropsch reactions lead to a net decrease in the number of moles present in the system, higher pressures lead to higher equilibrium conversions. High pressures also prevent slurry liquid loss due to vaporization. Equipment costs in general increase with pressure. The existing slurry system was designed for a maximum operating pressure of 350 psig; however, the mass flowmeters were factory calibrated at 200 psig maximum. On the other end of the scale, Fischer-Tropsch packed bed reactors have been successfully operated at atmospheric pressure, although most studies involving slurry reactors have been conducted in the range of 130 to 200 psig. A mid-range pressure of 160 psig was subsequently used during catalyst testing.

A wide range of flowrates have been used in previous slurry reactor studies. A diagram of slurry reactor flow regimes appears in Figure 11. Homogeneous

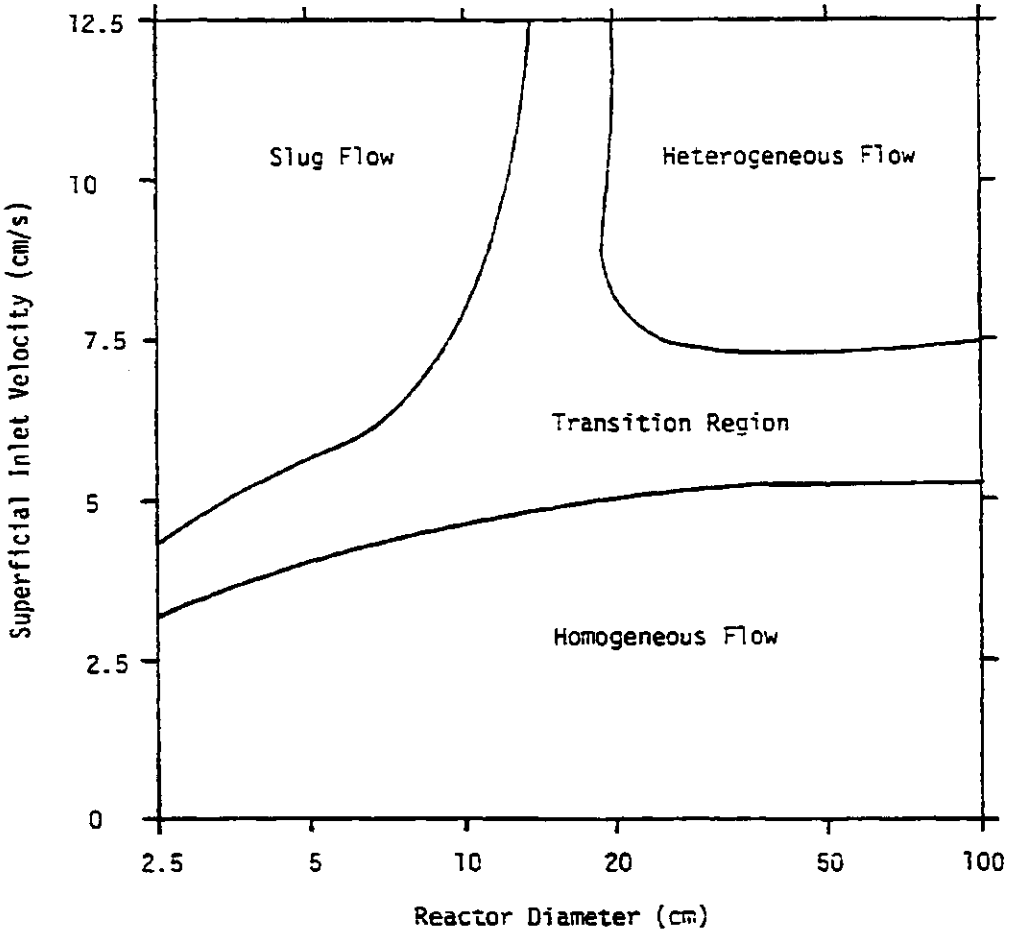


Figure 11. Slurry reactor bubble flow regimes (11).

flow, characterized by bubbles of uniform size rising undisturbed through the column, is used most often in smaller diameter reactors. Higher flowrates leads to slugging, which should be avoided (11). In this study, inlet flowrates were limited by equipment capacity, rather than by the selection of the most desirable flowrate. With the fixed feed composition, at 260°C and 160 psig, the maximum superficial velocity possible using the existing mass flowmeters was 1 cm/sec. This velocity was used throughout the study.

According to data presented by Kolbel (28), the 1 cm/sec inlet velocity is high enough to prevent catalyst sedimentation, but not so high as to cause slugging. Besides the flowrate, catalyst sedimentation depends on the catalyst particle size, density, and concentration, and properties of the slurry liquid. There are no penalties for using small catalyst sizes in slurry reactors, so they are ground as finely as possible. In this study, catalyst grinding and screening was performed manually, so the smallest practical limit was 200 - 270 mesh (53 - 74 microns), which was used in all experiments. Catalyst concentrations range from 5 to 20% by weight of the slurry in other slurry reactor studies. A 10% catalyst concentration was chosen as a base value in this study, which Kolbel felt was the optimum catalyst concentration.

Chevron Refined Wax 143, a mixture of C_{22} through C_{44} paraffins, was used as the slurry liquid in all of the catalyst tests. Paraffin waxes are popular slurry liquids, and the Chevron wax was chosen because it is a readily available, high boiling wax that is relatively pure and easy to analyze on gas chromatographs. The composition of Chevron Refined Wax 143 appears in Figure 12. A summary of the fixed catalyst testing conditions appears in Table 5, along with a comparison to the operating conditions used in other slurry Fischer-Tropsch reactor studies.

Before testing, all catalysts were reduced at synthesis temperature and pressure, i.e., 260°C and 160 psig. Pure hydrogen, at a superficial velocity of 1.2 cm/sec, was used as the reducing gas. The yields of liquid organic product, referenced to the weight of the catalyst in the reactor, was used as the criteria for catalyst comparison. The steady state yields of the five iron catalysts tested are compared in Figure 13.

The two unsupported catalysts behaved very similarly. The catalysts gave low yields of C_7 through C_{27} product, with Schulz-Flory constants (α) of about 0.82.

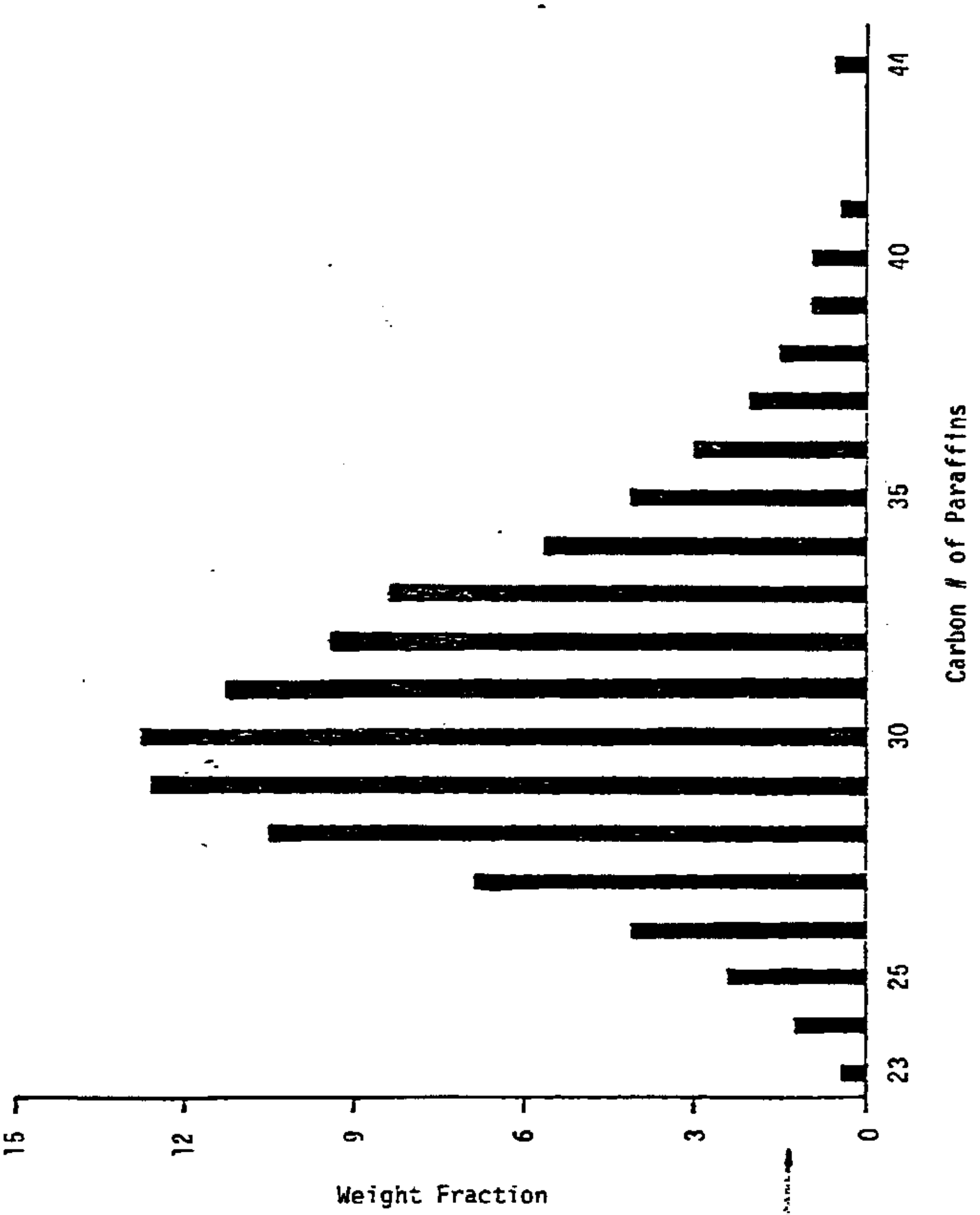
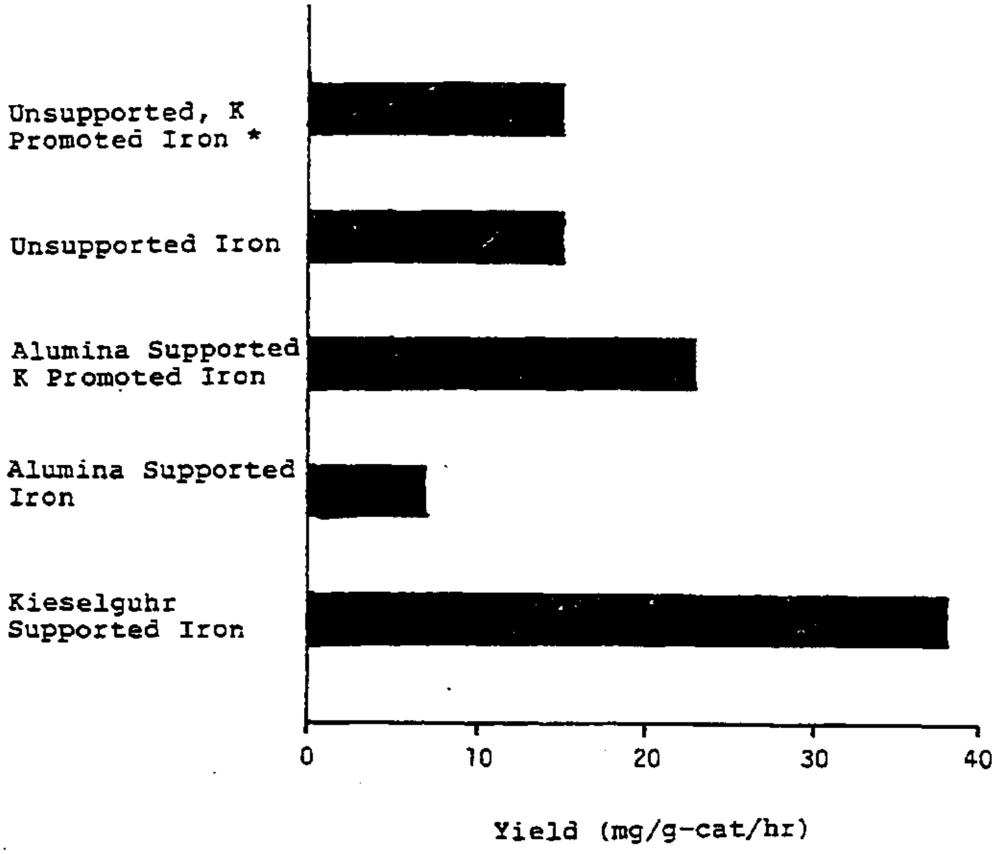


Figure 12. Composition of Chevron Refined Wax 143.

Table 5. Summary of fixed operating conditions for catalyst testing and comparison to other slurry studies.

Researcher	Temperature (°C)	Pressure (psig)	Gas Composition (mole %)	Superficial Inlet Velocity (cm/sec)	Catalyst Concentration (wt %)	Catalyst Type
This Study	260	160	Hydrogen - 26 Carbon Monoxide - 32 Carbon Dioxide - 16 Methane - 13 Ethylene - 13	1.0	10	Various Precipitated Iron
Kolbel Lab Reactor (28)	266	145	Hydrogen - 40 Carbon Monoxide - 60	3.5	10	Precipitated Iron
Rheinpreussen Demonstration Plant (28)	260	160	Hydrogen - 40 Carbon Monoxide - 60	9.5	12	Precipitated Iron
Mitra and Roy (37)	240-260	100-150	Hydrogen - 50 Carbon Monoxide - 38 Carbon Dioxide - 6 Nitrogen - 6	1.5-2.2	16-18	Precipitated Iron on Kieselguhr
Farley and Ray (21)	260-280	150	Hydrogen - 40 Carbon Monoxide - 60	7.3	12-13	Precipitated Iron
Deckwer, et al (13)	282-303	160	Hydrogen - 30/58 Carbon Monoxide - 70/42	.8-9	13.8	Precipitated Iron/Manganese



T = 260°C * T = 280°C

P = 11.8 atmospheres.

Figure 13. Comparison of yields obtained during catalyst testing.

The product composition is illustrated in Figure 14. These catalysts were very difficult to reduce in the slurry phase, with reduction times up to 24 hours. High yields of water and carbon dioxide were observed during startup, with little or no liquid organic product formed. Over a period of 6 to 8 hours, the carbon dioxide yields dropped while the organic yields increased. These yield trends were observed for all of the iron catalysts tested.

There was difficulty maintaining the initial activity for the test of the potassium promoted, unsupported catalyst. The temperature of the reactor was increased 20°C in order to maintain acceptable gas conversions. A material balance on the slurry liquid indicated that carbon may have formed during the startup, resulting in an initial loss of activity.

The unpromoted, alumina supported catalyst gave the lowest yields of all catalysts tested. There was no indication of activity losses during the test. The ability to increase the activity and the selectivity towards higher hydrocarbons by increasing the "basicity" of iron catalysts is well known (1,2,54). Since alumina has acidic properties, it has been suggested that it is a poor support for iron Fischer-Tropsch catalysts (20).

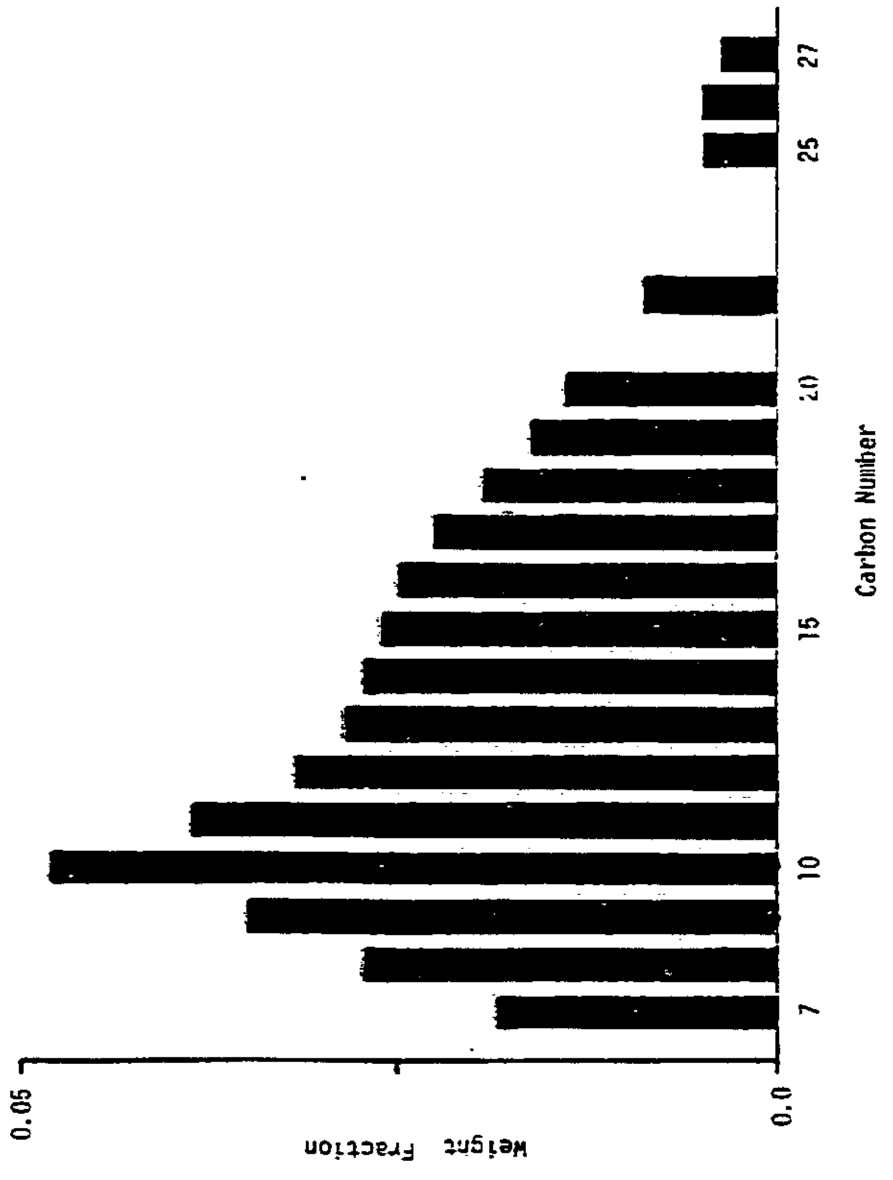


Figure 14. Liquid product C_7+ carbon number distribution for unsupported iron.

Increasing the alumina supported catalyst's basicity by promotion with potassium increased yields and conversions significantly. The yield of liquid organic product obtained using the promoted, alumina supported catalyst was three times that of the unpromoted catalyst. The product distributions, shown in Figures 15 and 16, was shifted slightly towards the heavier hydrocarbons for the promoted catalyst.

The test of the kieselguhr catalyst produced yields and conversions higher than any of the other iron catalysts. Also, the product was shifted towards low molecular weight products. This result was not unexpected due to reports in the literature (1,2,54). The product composition, Figure 17, is much lighter than that of the other iron catalysts tested. The product had an estimated API gravity of 55°, and a calculated cetane index of 47. These values were calculated using the correlations (23,36):

$$^{\circ}\mathrm{API} = 141.5/s - 131.5 \qquad [14]$$

$$\begin{aligned}\text{Cetane Index} = {} & 454.74 - 1641.416d + 774.74d^2 \\ & - 0.554b + 97.803(\log b)^2 \qquad [15]\end{aligned}$$

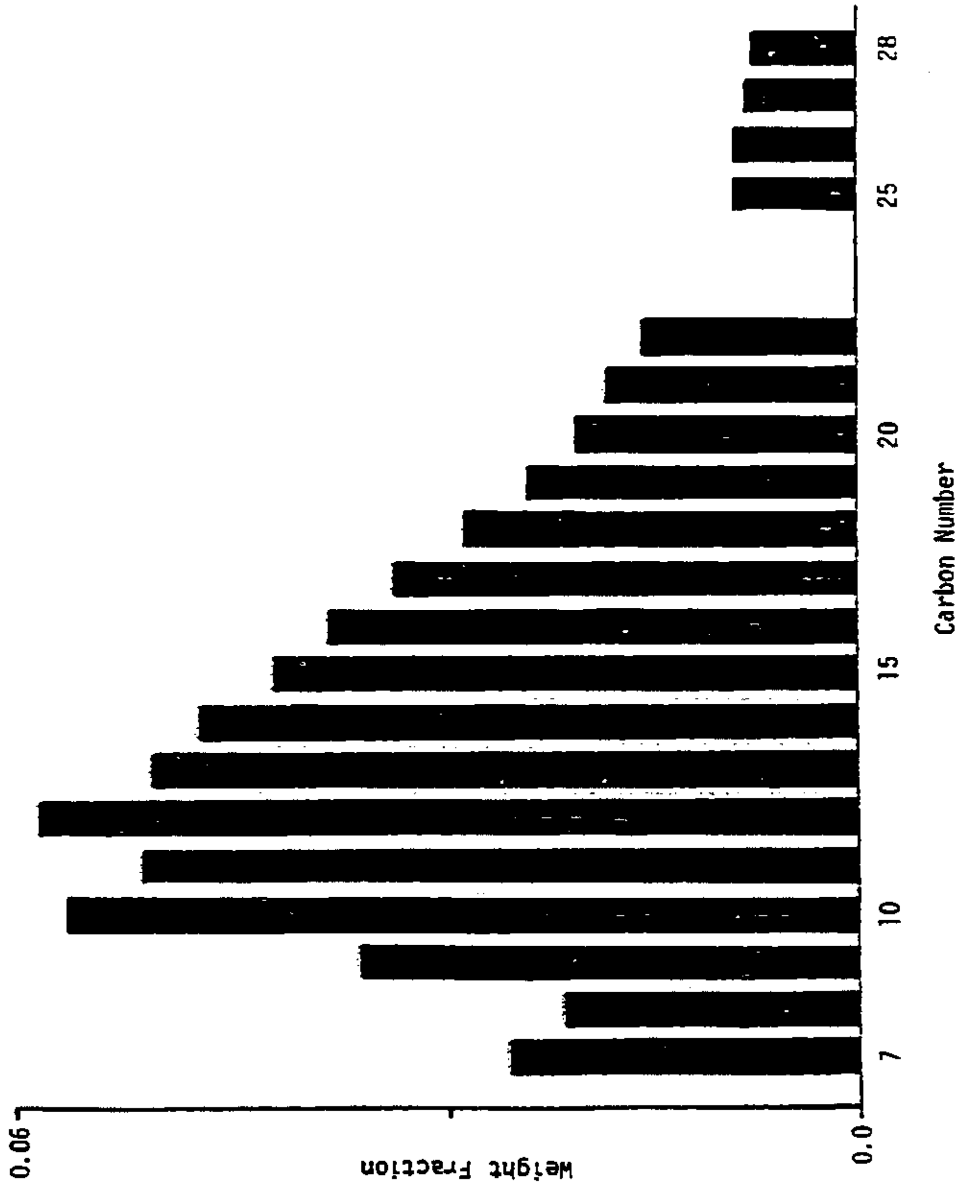


Figure 15. Liquid product C_7+ carbon number distribution for iron on alumina.

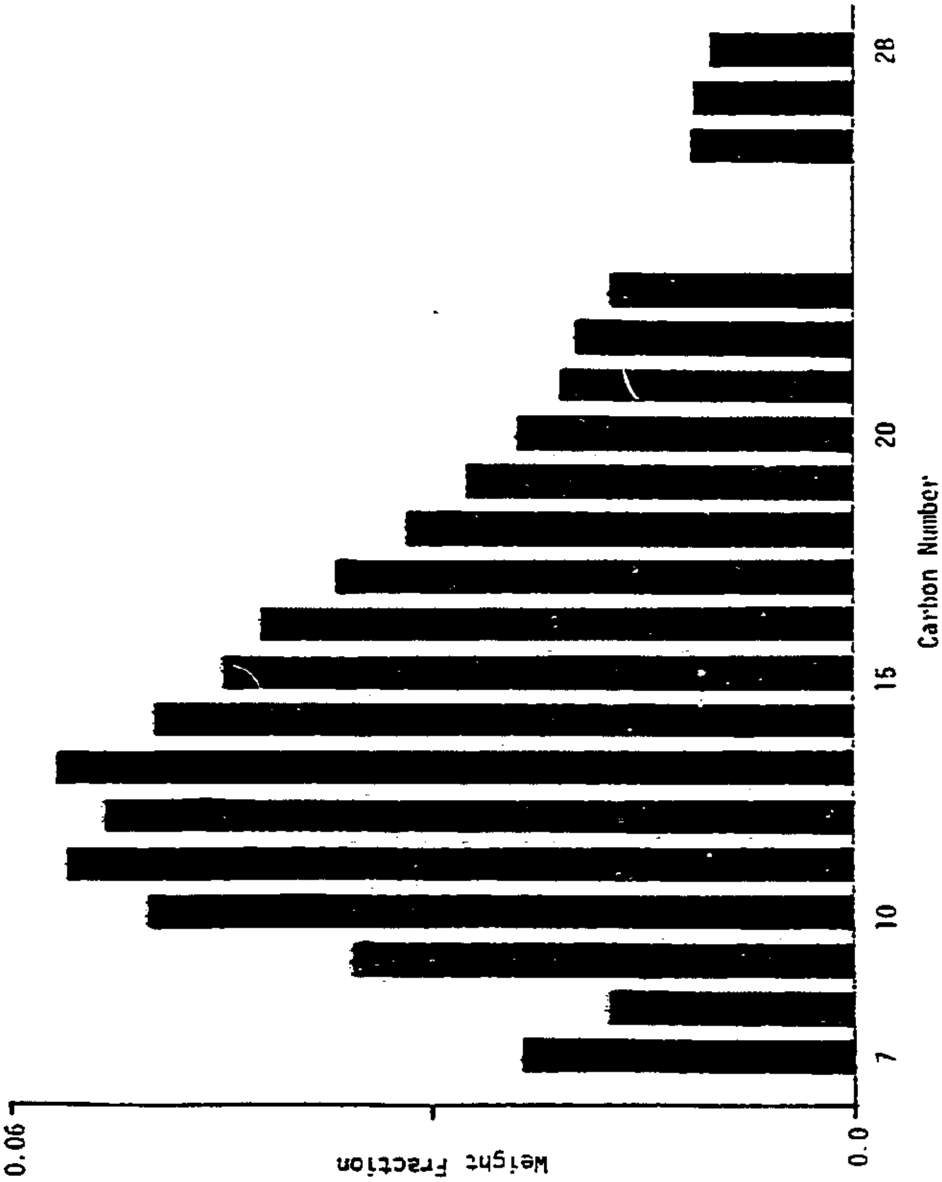


Figure 16. Liquid product C_7+ carbon number distribution for iron promoted with potassium on alumina.

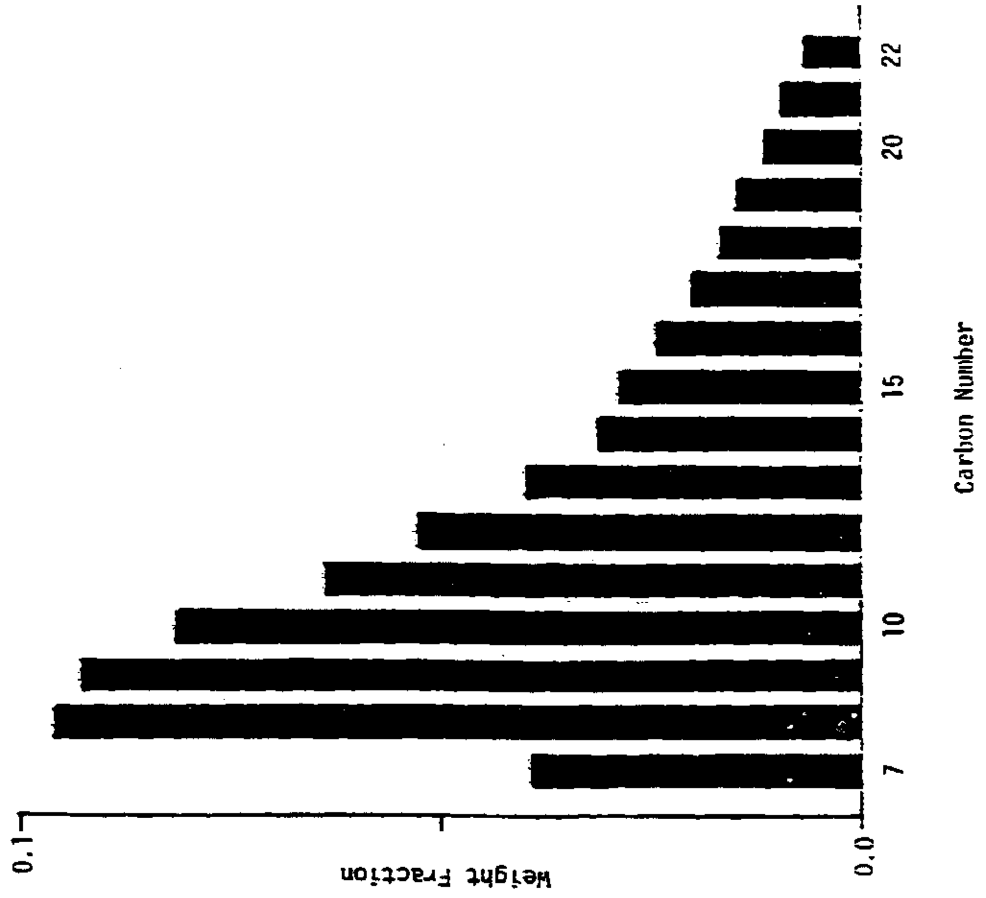


Figure 17. Liquid product C_7+ carbon number distribution for iron on kieselguhr.

s = specific gravity at 60°F

d = density in g/ml

b = 50% boiling point in °C

By contrast, kerosine has an API gravity of about 43° and a cetane index between 48 and 51. JP-4 has an API gravity between 53° and 55° with a cetane index between 46 and 48 (58).

For the purposes of comparison, a test was made using the standard cobalt-alumina catalyst under the same conditions used for the iron catalysts. The yields were much higher than for the iron-kieselguhr catalyst: 144 mg/g-cat/hr for cobalt as opposed to 38 mg/g-cat/hr for iron. The product composition from cobalt, Figure 18, was similar to that of the iron-kieselguhr catalyst in that it was much lighter than the product from the other iron catalysts. The carbon monoxide conversion over the cobalt catalyst was only 5%; apparently all or most of the synthesis product was derived from ethylene. Over iron catalysts, ethylene was always either a net product of the synthesis, or it was reduced to ethane. The incorporation of ethylene into the synthesis products over iron catalysts was not observed.

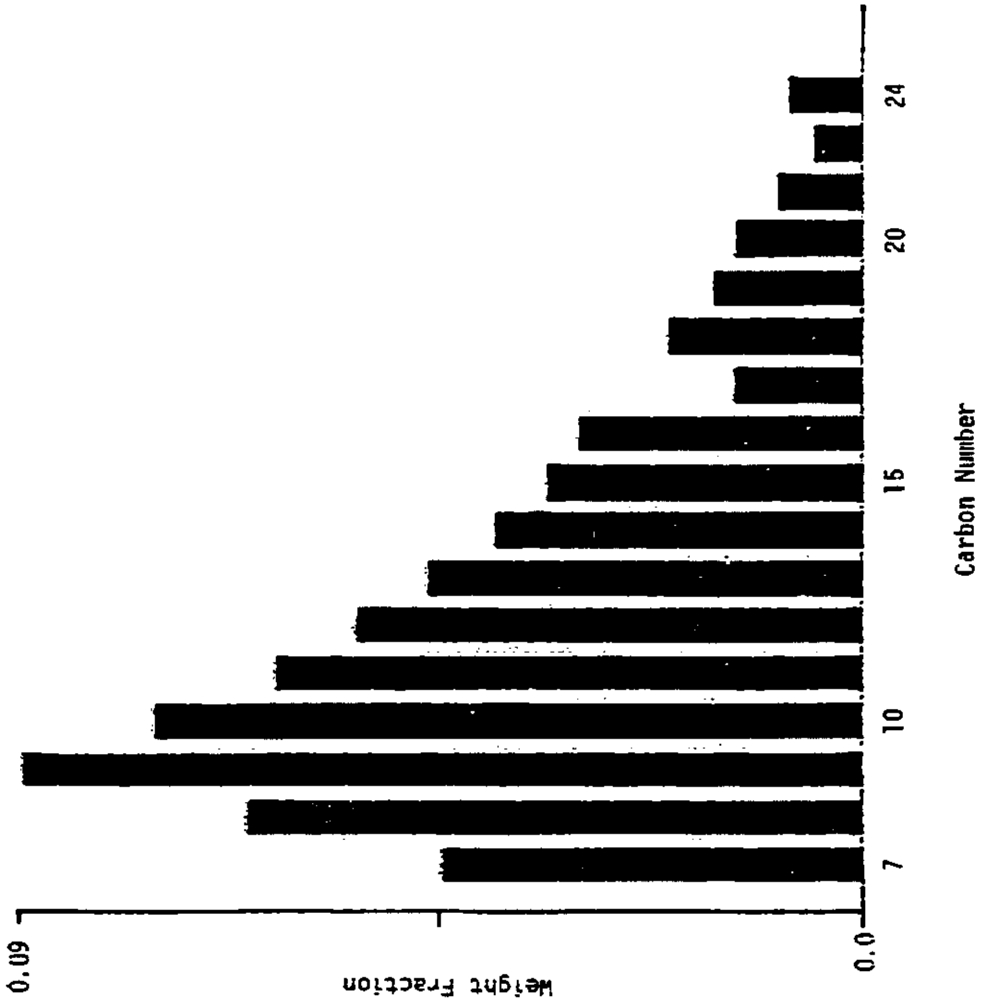


Figure 18. Liquid product C_7+ carbon number distribution for cobalt on alumina.

2. Slurry Liquid Testing.

Using product yields as the criteria, the iron-kieselguhr catalyst was chosen as the best iron catalyst for use in the continuing investigation. Since ethylene in the feed gas did not lead to higher yields over the iron catalysts, as it does over cobalt, an effort was made to find a simulated pyrolysis gas composition which had higher hydrogen and carbon monoxide concentrations at the expense of non-reactive components. The variation in pyrolysis gas composition with the molar hydrogen/carbon monoxide ratio appears in Figure 19. In turn, the hydrogen/carbon monoxide ratio depends on the pyrolyzer temperature and its steam feed rate.

Tests using the iron-kieselguhr/Chevron Refined Wax 143 combination revealed that the liquid yields did not vary strongly with the hydrogen/carbon monoxide feed ratio. The individual hydrogen and carbon monoxide conversions varied as expected, as shown in Figure 20. Since higher partial pressures of hydrogen should help prevent carbon formation within the reactor during synthesis, a hydrogen/carbon monoxide ratio of 2.8, the highest ratio tested, was used during liquid testing. Lumping the low concentrations of ethylene and other

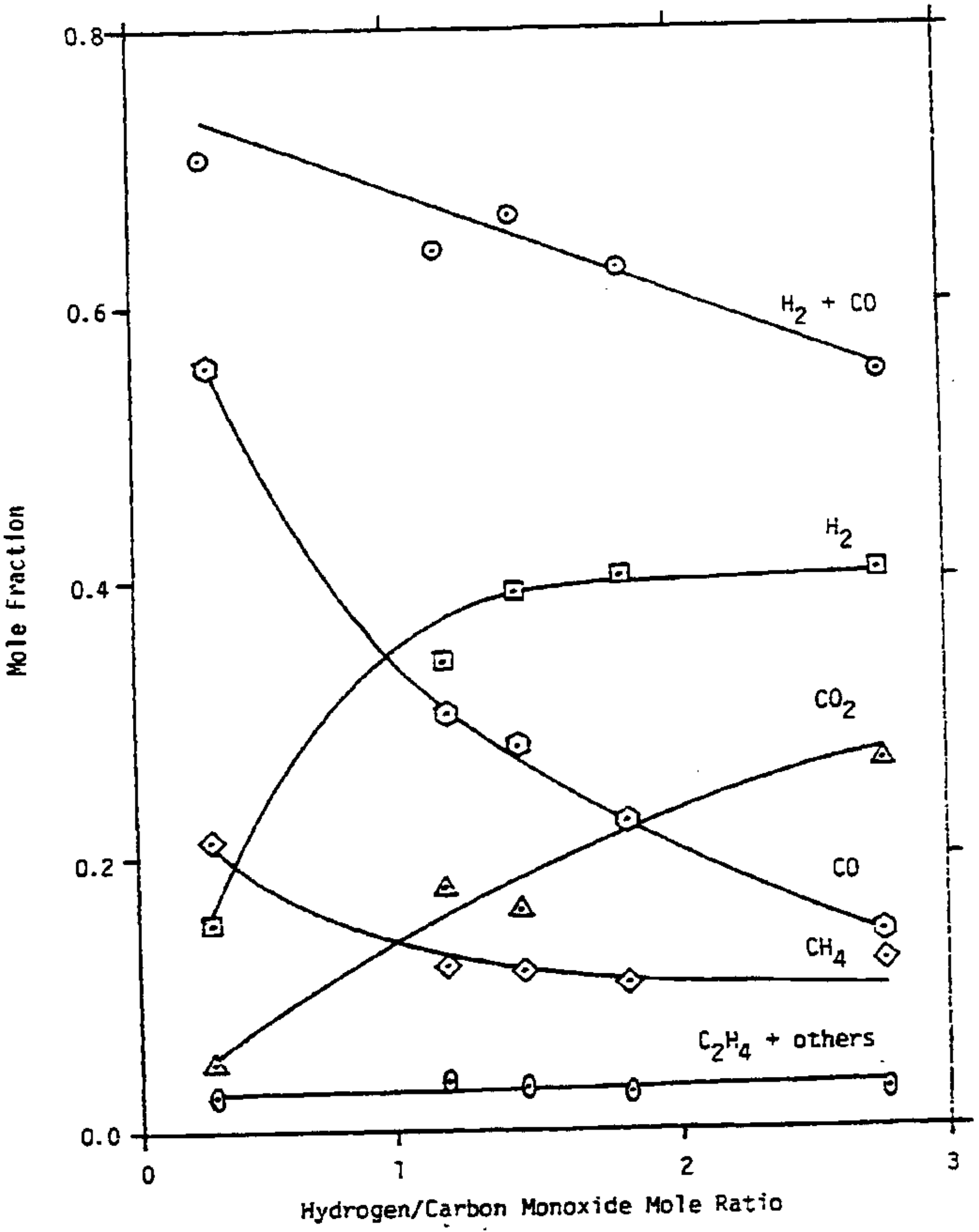


Figure 19. Pyrolysis gas composition from sawdust pyrolysis as a function of the H_2/CO ratio. Data from LSIU Runs 311B, 311D, 401A, 401C, and (31).

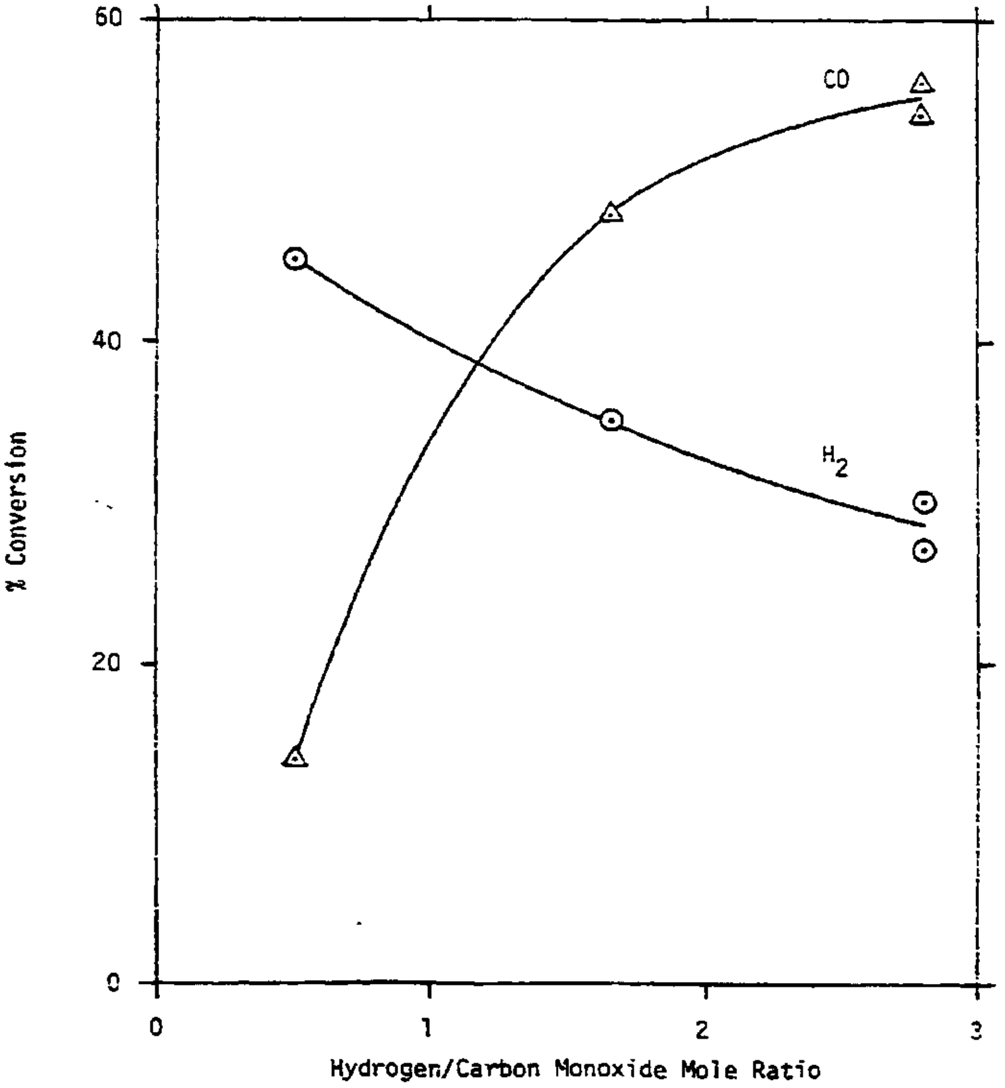


Figure 20. Hydrogen and carbon monoxide conversions as a function of the H_2/CO feed ratio.

trace components into the methane fraction, the composition of the simulated pyrolysis gas used during liquid testing was 41.1 mole % hydrogen, 14.7 % carbon monoxide, 27.5 % carbon dioxide, and 16.7 methane. All other operating conditions were identical to those used during catalyst testing.

In addition to Chevron Refined Wax 143, five additional liquids were tested: two silicon liquids - Syltherm 800 Heat Transfer Liquid and Dow Corning 210H Fluid; two pure paraffins - normal hexadecane (C_{16}) and normal eicosane (C_{20}); and Fischer-Tropsch organic product obtained from large scale fluidized bed runs using cobalt-alumina catalyst.

The silicone liquids were chosen primarily because of their low vapor pressure at elevated temperatures. Syltherm 800 is a silicone polymer, (dimethylpolysiloxane), normally used as the liquid media in heat transfer systems operating up to 399°C (18). It is intended to be used in inert environments and is sensitive to contamination and oxidation. Degradation of Syltherm 800 leads to the formation of lower molecular weight products. When this liquid was tested, large amounts of liquid were recovered in the product traps