

## Executive Summary

### CAER

Steady-state supercritical Fischer-Tropsch synthesis was studied using a fixed-bed reactor and a Co/SiO<sub>2</sub> catalyst. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain valid comparisons.

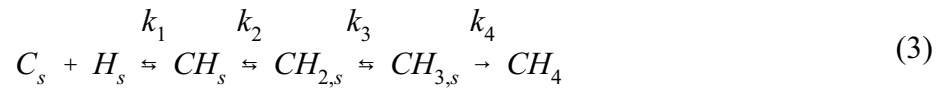
Three different partial pressure points of the mixture were chosen based on the density-pressure curve to investigate the pressure tuning effect for Fischer-Tropsch synthesis near critical region. It was found that supercritical phase Fischer-Tropsch synthesis can significantly inhibit the deactivation of catalyst due to the extraction of heavy hydrocarbon products from catalyst pores and possibly improving the heat transfer in plug-flow reactor. The highest CO conversion was obtained when the solvent partial pressure is just above its critical pressure compared to its more gas-like or liquid-like state. Reproducible data were obtained by repeating the conditions.

Methane and carbon dioxide selectivity decreased dramatically with an increase of pentane-hexane partial pressure. The selectivity of reaction and  $\alpha$  value of different conditions will be defined in future work.

The vapor-liquid equilibrium has the potential to dramatically impact the results for slurry bubble column operations (e.g., last quarterly report). Data are not available to allow one to assess the impact of vapor-equilibrium on the slurry reactor operation. To obtain data to evaluate this effect, we have synthesized deuterated FT products to add during synthesis with H<sub>2</sub>/CO in order to obtain retention times in the reactor for various carbon number products and thereby obtain experimental values for vapor-liquid under reaction conditions. These results will greatly aid in reactor design and in the evaluation of various separation procedures. In addition, these

studies allow us to compare isotopic data from the CAER CSTR with those obtained at Berkeley in fixed bed reactors. These studies also serve to integrate the research activities of the two labs.

The isotope effect with deuterium is probably the combination of equilibrium and kinetic effects. The proposed steps for the hydrogenation of carbon monoxide are:



It has been proposed that the rate determining step of the FT synthesis is the hydrogenation of one of the surface carbon species shown in equation six, where  $k_1$ ,  $k_2$  or  $k_3$  are rate constants.

Equations 1 and 2 are assumed to be at equilibrium. The rate of product formation is:

$$R(P) = k_x \theta_c \theta_H^x \quad (4)$$

where  $x$  is the number of H in in the  $CH_x$  species formed during the rate determining step. Under typical FT conditions, it is assumed that  $\theta_c \approx 1$  and  $\theta_H$  is determined by the equilibrium constant ( $K_H$ ) for dissociative chemisorption of  $H_2$  and the competition for vacant sites by CO and  $H_2$ .

The surface coverage of H is given by:

$$\theta_H = K_H^{1/2} P_{H_2}^{1/2} (1 + bP_{CO})^{-1/2} \quad (5)$$

and the rate of product formation is equal to:

$$R(P) = k_1 K_H^{1/2} P_{H_2}^{1/2} (1 + bP_{CO})^{-1/2} \quad (6)$$

where  $x$  and  $\theta_c$  from equation 4 are both equal to 1. It is generally accepted that  $k_{1,H} > k_{1,D}$  and  $K_D > K_H$ . Switching from  $D_2$  to  $H_2$  would effect both  $k_1$  and  $K_{H(D)}$  in opposite directions so whether there is an inverse, normal or no isotope effect would depend on the magnitude of change in  $k_1$  and  $K_{H(D)}$ .

### UC/B

In this reporting period, we continued our X-ray absorption spectroscopic (XAS) studies at the Stanford Synchrotron Radiation Laboratory (SSRL) with emphasis on Fe K-edge measurements on our standard samples and on a series of fresh and used Fe-Si catalysts provided by Dr. Burtron A. Davis at the Center for Applied Energy Research (CAER) of University of Kentucky. We measured the XAS spectra of standard compounds:  $Fe_2O_3$ ,  $Fe_3O_4$ ,  $FeO$ ,  $ZnFe_2O_4$  and  $Fe_xC$ . We also investigated the *in-situ* reduction and carburization behavior of  $Fe_2O_3$  in synthesis gas. In addition, we measured five samples from CAER that consisted of unpromoted precipitated Fe oxides (RJO 249) and its samples used for various lengths of time for FTS (RJO282C, D, G and J).

We have also investigated the isotopic effects using synthesis gases of  $D_2/CO/N_2$  (62/31/7) and  $H_2/CO/N_2$  (62/31/7) on an Fe-Zn catalyst ( $Zn/Fe=0.1$ ,  $K/M=0.02$ ,  $Cu/Fe=0.01$ ) at  $235^\circ C$  and 21.4 atm. Compared with the results using the synthesis gas of  $H_2/CO/N_2$ , lower methane and  $CO_2$  selectivities and a higher selectivity to  $C_{5+}$  were obtained with  $D_2/CO/N_2$ .

Inverse isotopic effects for CO conversion rate and hydrocarbon formation rate and a normal isotopic effect for  $CO_2$  formation were observed when  $D_2$  was used instead of  $H_2$ . The  $k_H/k_D$  ratio for hydrocarbon formation decreased with increasing CO conversion and with increasing carbon number, suggesting that isotopic effects were more evident for the formation of hydrocarbons with higher molecular weight, and for the formation of paraffins than for olefins.

In this quarter, an additional reaction pathway was studied for the Co-catalyzed FTS. We assumed that both H<sub>2</sub> and H<sub>2</sub>O promote the dissociation of adsorbed CO, which controls the CO consumption rate. Kinetic studies were carried out by running FTS reaction on a 21.9 wt.% Co/SiO<sub>2</sub> catalyst at 200°C. The reactants, CO (2.3-8.7 atm), H<sub>2</sub> (9.3-25.0 atm), and H<sub>2</sub>O (0.5-2.0 atm) in different molar ratios, were introduced into the reactor separately. CO conversion and selectivities of primary hydrocarbons (up to C<sub>12</sub>) were measured at steady states. The CO consumption rate data along with those obtained from the previous kinetic run were fitted to rate expressions on the basis of our proposed mechanisms with multivariable non-linear regression.

H<sub>2</sub>/D<sub>2</sub> isotope effects during FTS were studied by running the reactions with both CO/H<sub>2</sub> and CO/D<sub>2</sub> over a 21.9 wt.% Co/SiO<sub>2</sub> catalyst at 200°C and 20 atm. The kinetic isotope effects for CO consumption and for individual hydrocarbons C<sub>1</sub>-C<sub>7</sub> were obtained by comparing the corresponding reaction rates with H<sub>2</sub> and D<sub>2</sub>. Inverse kinetic isotope effects were obtained for CO consumption ( $k_H/k_D = 0.8$ ) when the CO conversions were between 10% and 40%. The results showed that the isotope effects ( $k_H/k_D$ ) were generally inverse for paraffins whereas normal for olefins at low conversions when the effect of secondary reactions could be neglected. These isotope effects resulted from a combination of kinetic and equilibrium isotopic effects which may be associated with individual elementary steps.

## **Task 1. Iron Catalyst Preparation**

The objective of this task is to produce robust intermediate- and high- $\alpha$  catalysts.

## **Task 2. Catalyst Testing**

The objective of this task is to obtain catalyst performance on the catalysts prepared in Task 1.

### **A. Deuterium Isotope Effects with a Precipitated Iron Catalyst in Slurry Phase Fischer-Tropsch Synthesis**

The impact of deuterium on the Fischer-Tropsch (FT) synthesis was studied with a precipitated iron catalyst in the slurry phase. As indicated in the summary, the data will provide design data for slurry reactors and separators. Deuterium has been used by several research groups to better understand the mechanism of CO hydrogenation. Inverse ( $k_H/k_D < 1$ ), normal ( $k_H/k_D > 1$ ) and no isotope effect ( $k_H/k_D = 1$ ) have been reported (1). The conflicting results are thought to arise because rate of reaction is a combination of kinetic and equilibrium factors (2).

### **Experimental**

Precipitated iron catalyst (100Fe/4.6Si/1.44K, atomic basis) (5g) was added to 310 g of Polywax 3000 (Petrolite, average M.W.=3000) which had been melted at 130°C in a one liter CSTR. The catalyst was activated with CO as follows. The reactor stirrer was set at 750 rpm, CO flow was started at 25 slph, the pressure was increased to 175 psig and the temperature was increased to 270°C at 2°C/min. These conditions were maintained for 24 hours and then the CO flow was lowered to 9.55 slph and D<sub>2</sub> flow was started at 6.52 slph. Fischer-Tropsch conditions were: whsv=5.0 sl h<sup>-1</sup> g-Fe<sup>-1</sup>, D<sub>2</sub>/CO=0.67, 270°C and 175 psig. Periodically D<sub>2</sub> was stopped and H<sub>2</sub> was used. The time on stream for each gas is shown in Table 1.

Table 1	
Time on Stream for D <sub>2</sub> and H <sub>2</sub>	
Time on stream (h)	Gas
0 - 137	D <sub>2</sub>
138 - 330	H <sub>2</sub>
331 - 384	D <sub>2</sub>
385 - 859	H <sub>2</sub>

H<sub>2</sub> or D<sub>2</sub> and CO flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 L mixing vessel, was delivered to the catalyst slurry through a dip tube that extended to below the impeller blade. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 60°C and 0°C. Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter (0.5 µm) and collected in a 200°C trap. Uncondensed effluent was fed to a multichannel on-line refinery gas analyzer (Hewlett Packard Quad Series Micro GC) for determination of CO, H<sub>2</sub>, D<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub> - C<sub>8</sub> alkanes and alkenes.

After 130 hours of FTS with D<sub>2</sub>, 25 ml of a solution of 5.0 g of 1-heptene (C<sub>7</sub>H<sub>14</sub>, Aldrich) and 5.0 g of 1-octene (C<sub>8</sub>H<sub>16</sub>, Aldrich) in decalin (Aldrich) were pumped into the reactor over a two hour period with a LDC/Milton Roy pump. Liquid samples were collected four hours and 24 hours after pumping the alkene mixture. Liquid samples will be analyzed by GC-MS to determine the relative rates of alkene isomerization and hydrogenation.

## Results and Discussion

Through the first 137 hours of FTS with D<sub>2</sub>, there was an induction period in which the syngas conversion gradually increased to 86% (Figure 1). During this time, 90.8 g of deuterated liquid hydrocarbon products were collected. The use of Polywax 3000 polyethylene, low vapor pressure under reaction conditions, as a slurry medium prevented the condensed liquid products from being contaminated with hydrogen containing compounds from the initial slurry medium.

During slurry phase FTS, a significant amount of product is held-up in the reactor which can influence the product distribution. Samples collected after D<sub>2</sub> was stopped will be analyzed by GC-MS to determine the reactor hold-up time of alkanes and alkenes as a function of carbon number.

Syngas conversion was stable after about 137 hours on stream and at this time D<sub>2</sub> was stopped and H<sub>2</sub> was started. There was a rapid decrease in syngas conversion from 86% to 78% during the first 24 hours after H<sub>2</sub> was started and during the next 200 hours (TOS=330 h), the syngas conversion gradually decreased to 74% (Figure 1). After this time, H<sub>2</sub> was stopped and D<sub>2</sub> was restarted. Switching back to D<sub>2</sub> caused the syngas conversion to increase to 83% within 24 hours of the change. Conversion remained constant for 48 hours and then H<sub>2</sub> was restarted. Once again the syngas conversion rapidly decreased after D<sub>2</sub> was stopped and H<sub>2</sub> was started.

The FT rate responded similarly as the syngas conversion (Figure 2); however, the water-gas shift (WGS) rates increased only slightly after changes from D<sub>2</sub> to H<sub>2</sub> were made (Figure 3).

The FT and WGS rates are defined as follows:

$$r_{FT} = r_{CO} - r_{CO_2} \quad (1)$$

$$r_{WGS} = r_{CO_2} \quad (2)$$

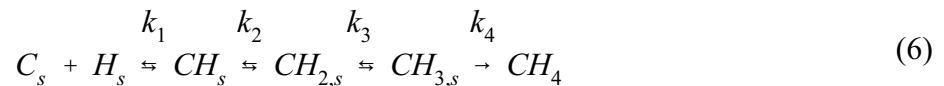
where  $r_{CO}$  is the rate of CO conversion and  $r_{CO_2}$  is the rate of CO<sub>2</sub> formation. When the switch from H<sub>2</sub> to D<sub>2</sub> was made after 330 hours on stream, the FT rate increased from 0.054 to 0.064 mol h<sup>-1</sup> g-Fe<sup>-1</sup> and the WGS rate increased from approximately 0.044 to 0.047 mol h<sup>-1</sup> g-Fe<sup>-1</sup>. There was significant variance in the WGS shift data (Figure 3); however, it is clear that the WGS rate decreased after the initial switch from D<sub>2</sub> to H<sub>2</sub> was made and increased when the switch from H<sub>2</sub> to D<sub>2</sub> was made. The isotope effect ( $k_H/k_D$ ) observed for the FT rate was 0.85 and approximately 0.93 for the WGS rate.

There was also an isotope effect observed for CH<sub>4</sub> selectivity and alkene selectivity. CH<sub>4</sub> selectivity is defined as follows:

$$CH_4sel = \frac{r_{CH_4}}{r_{FT}} \times 100 \quad (3)$$

where  $r_{\text{CH}_4}$  is the rate of  $\text{CH}_4$  production. Figure 4 shows that the methane selectivity increased steadily from approximately 5% to 20% throughout the run. A decrease in the  $\text{CH}_4$  selectivity from 9.0% to 7.4% was observed when  $\text{H}_2$  was switched to  $\text{D}_2$  after 330 hours on stream. This is a relative decrease of 18%. When  $\text{D}_2$  was switched back to  $\text{H}_2$  the  $\text{CH}_4$  selectivity increased to 9.7%. Similar trends were observed for  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  alkene selectivity (Figure 5) which is defined as the molar ratio, alkene/(alkene+alkane). Initially the alkene selectivity decreased as the syngas conversion increased during the first 137 hours on stream. After the conversion stabilized, the  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  alkene selectivity were 0.11, 0.69, and 0.74, respectively. Switching from  $\text{H}_2$  to  $\text{D}_2$  caused the  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  alkene selectivity to increase to 0.19, 0.73, and 0.77, respectively. This corresponds to relative increases of 73%, 6% and 4% for the  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  alkene selectivity, respectively.

The isotope effect with deuterium is probably the combination of equilibrium and kinetic effects (2-4). The proposed steps for the hydrogenation of carbon monoxide are:



It has been proposed that the rate determining step of the FT synthesis is the hydrogenation of one of the surface carbon species shown in equation six, where  $k_1$ ,  $k_2$  or  $k_3$  are rate constants (2). Equations 4 and 5 are assumed to be at equilibrium. The rate of product formation is:

$$R(P) = k_x \theta_C \theta_H^x \quad (7)$$

where  $x$  is the number of H in in the  $\text{CH}_x$  species formed during the rate determining step. Under typical FT conditions, it is assumed that  $\theta_C \approx 1$  and  $\theta_H$  is determined by the equilibrium constant



( $K_H$ ) for dissociative chemisorption of  $H_2$  and the competition for vacant sites by CO and  $H_2$ .

The surface coverage of H is given by:

$$\theta_H = K_H^{1/2} P_{H_2}^{1/2} (1 + bP_{CO})^{-1/2} \quad (8)$$

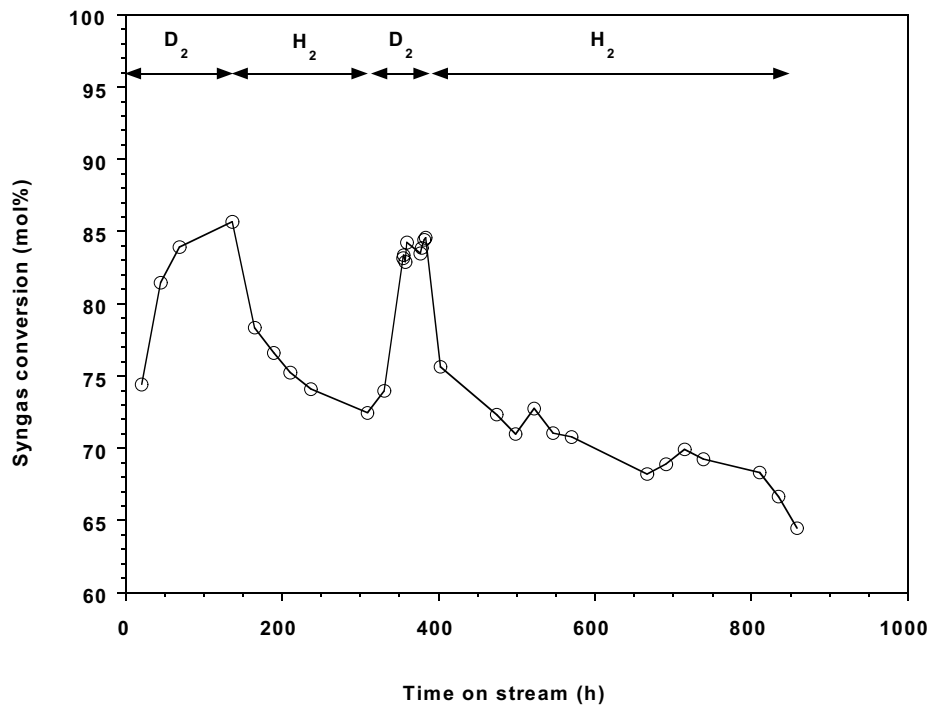
and the rate of product formation is equal to:

$$R(P) = k_1 K_H^{1/2} P_{H_2}^{1/2} (1 + bP_{CO})^{-1/2} \quad (9)$$

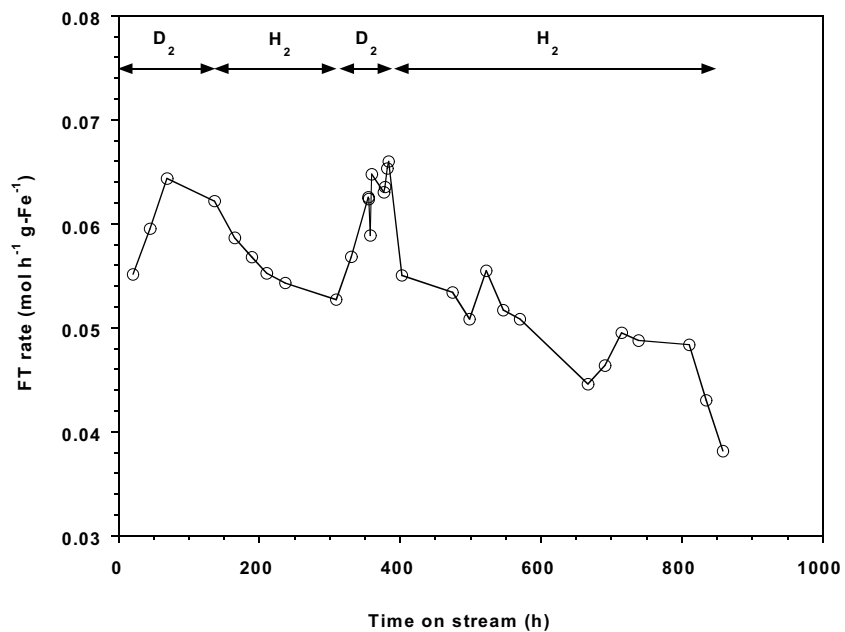
where  $x$  and  $\theta_C$  from equation 7 are both equal to 1(2). It is generally accepted that  $k_{1,H} > k_{1,D}$  and  $K_D > K_H$ . Switching from  $D_2$  to  $H_2$  would effect both  $k_1$  and  $K_{H(D)}$  in opposite directions so whether there is an inverse, normal or no isotope effect would depend on the magnitude of change in  $k_1$  and  $K_{H(D)}$ .

### References

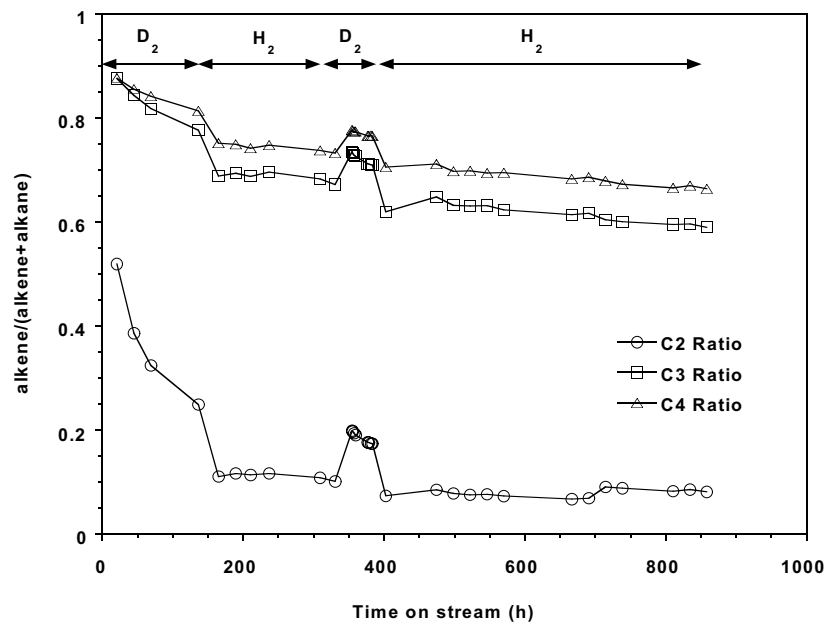
1. A. Raje and B. H. Davis. Fischer-Tropsch Synthesis. Mechanism Studies Using Isotopes. In *Catalysis*; J. J. Spivey, Ed.; The Royal Society of Chemistry; 1996; Vol. 12.
2. T. P. Wilson, *J. Catal.*, 1979, **60**, 167.
3. C. S. Kellner and A. T. Bell, *J. Catal.*, 1981, **67**, 175.
4. M. A. Logan and G. A. Somorjai, *J. Catal.*, 1985, **95**, 317.



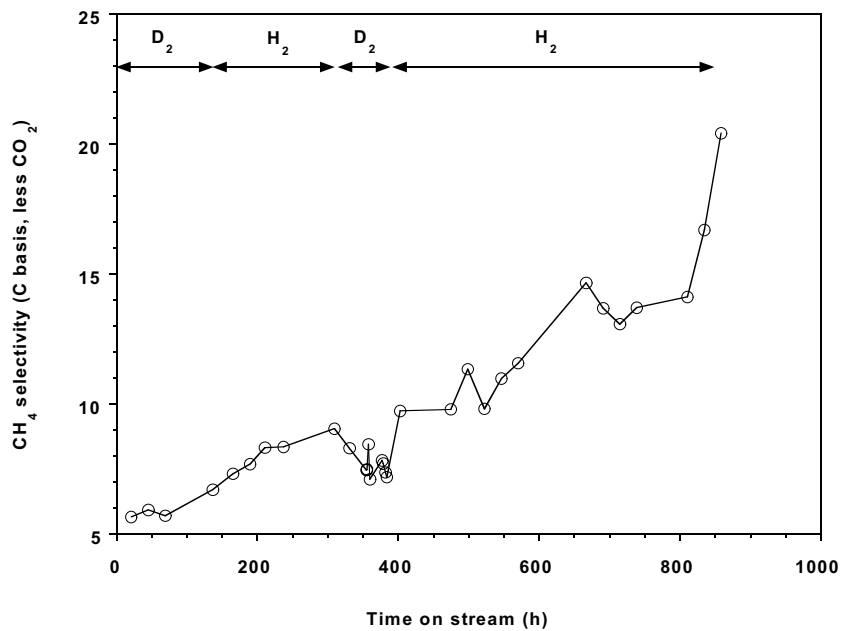
**Figure 1.** Syngas conversion as a function of time on stream.



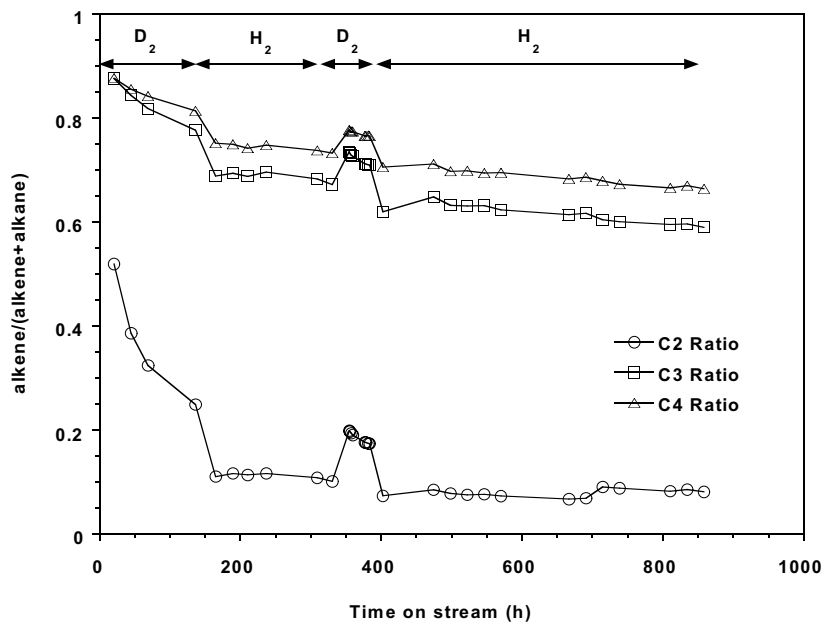
**Figure 2.** Effect of deuterium on FT rate.



**Figure 3.** Effect of deuterium on C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> alkene selectivity.



**Figure 4.** Effect of deuterium on CH<sub>4</sub> selectivity.



**Figure 5.** Effect of deuterium on C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> alkene selectivity.

## **B. Reactor Engineering — CSTR Mixing Study**

In a CSTR slurry reactor, the concentration distribution of solid catalyst in the reactor liquid significantly affects the reaction conversion. The catalyst dispersion is related to the liquid rotation speed under agitation. A cold mold test of our CSTR reactor (1 liter) was conducted in the absence of baffle to examine how liquid speed responds to agitation speed. About 300 gram of C30 oil was used as medium with a small ball (2 mm diameter) placed on liquid surface to measure the liquid rotation speed. The mixing apparatus and dimensions are shown schematically in Figure 1.

It was observed that the ball did not reside on a radial position close to the tank wall as expected. Instead, the orbit of the ball was relatively irregular, spanning from the agitator shaft and inner tank wall. Therefore, the measured liquid speed was interpreted as the average speed in the tank, rather than at a fixed radial position. Figure 2 shows the measured liquid speed vs. agitation speed, both in terms of rpm.

The lowest agitation speed used in this test was 610 rpm, which corresponds to a mixing Reynold's number of 2200. Thus all the mixing tests are under turbulent conditions. According to an empirical correlation available in literature for large agitation tank, the distribution of linear liquid velocity (cm/s) and liquid rotation speed (rpm) can be calculated as shown in Figure 3 for agitation speed of 1040 rpm. The measured liquid speed is equivalent to that at the radial position of  $r/R = 0.47$ . This value also applies to the other tests. It should be noted that the literature correlation is for large agitation tanks and when liquid velocity is not a function of axial position. In our test, the ball stays on liquid surface which is actually a convex and the convexity changes with agitation speed. In the absence of the baffle, the liquid rotation approaches that of the stirrer. Even with the baffles, the liquid rotation should be greater than half that of the stirrer.

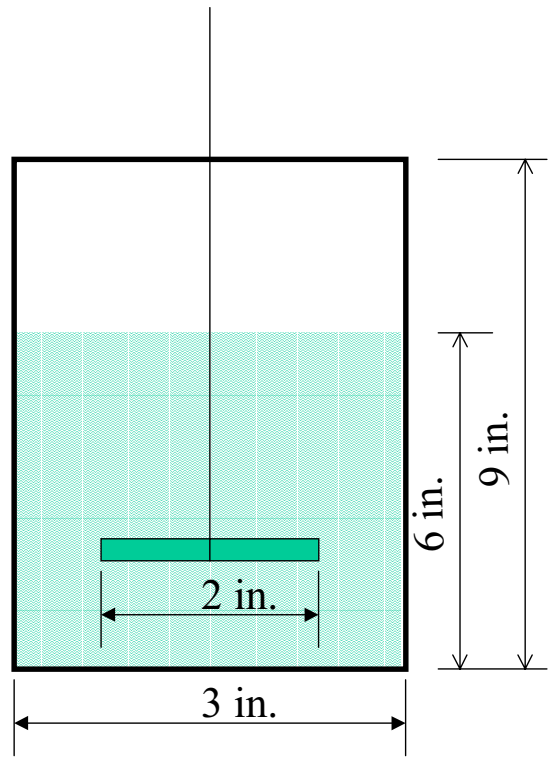


Figure 1 Agitation Apparatus



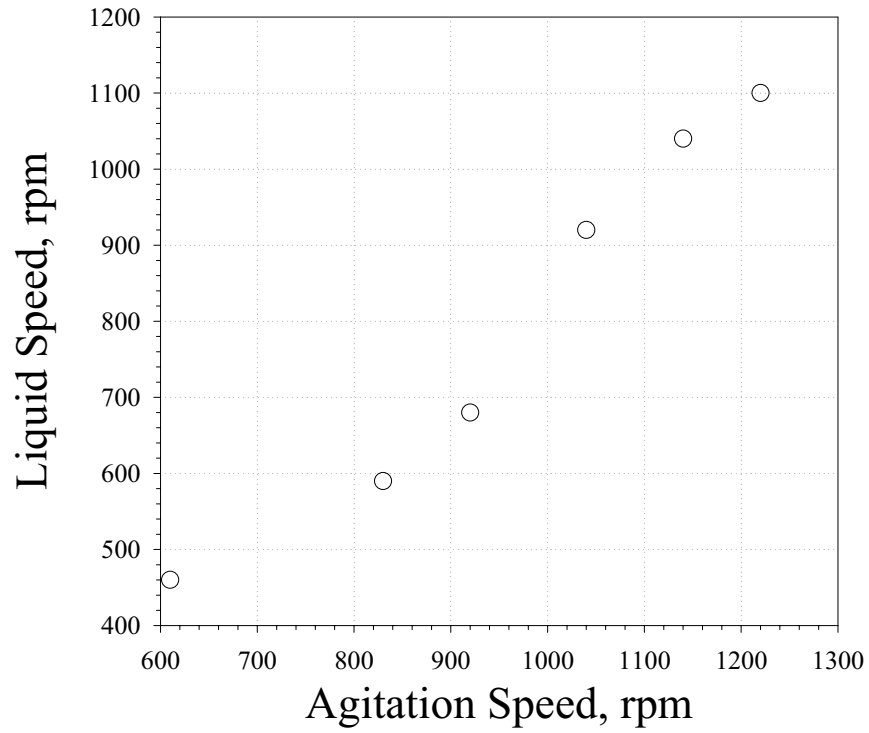


Figure 2 Measured liquid speed vs. agitation speed

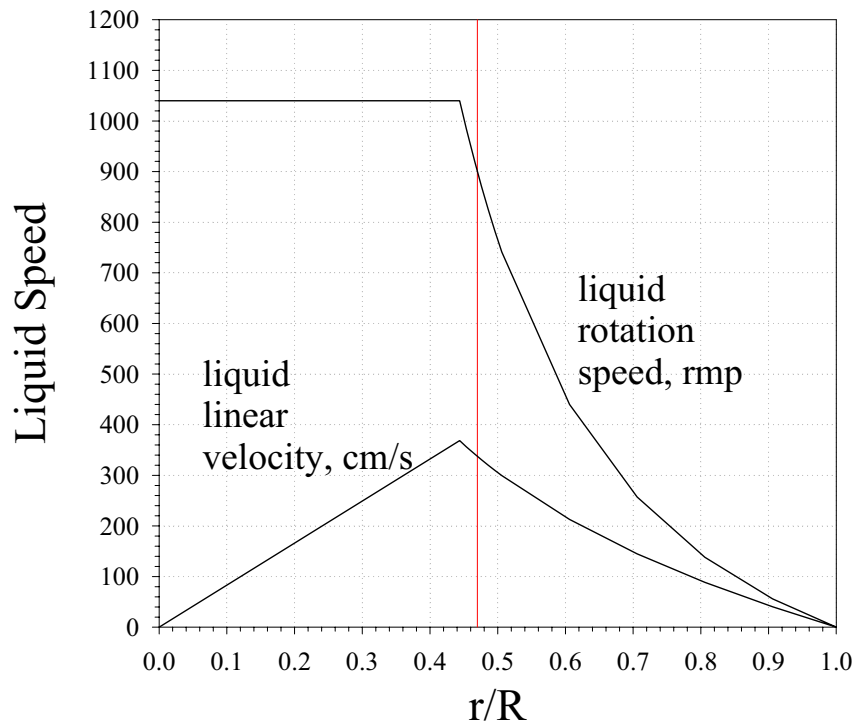


Figure 3 Liquid speed distribution in the tank

### **Task 3. Catalyst Characterization**

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

No scheduled or further activity to report.

### **Task 4. Wax/Catalyst Separation**

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

A meeting with Pall officials is scheduled for November 8, 1999. It is anticipated that a joint research project will be defined during this meeting. This follows a previous meeting with Pall, the CAER P.I. and two companies who were interested in separations.

### **Task 5. Oxygenates**

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

No scheduled or further activity to report.

### **Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts**

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

Literature is being compiled to augment the current report on this task.

### **Task 7. Co Catalyst Preparation**

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

Supports have been obtained as well as those prepared at the CAER to sue to prepare supported catalysts.

### **Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations**

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

A run in the CSTR has been completed that allows the comparison of the productivity of a cobalt catalyst in a CSTR and a supercritical fixed-bed reactor. To a first approximation, the productivity/g catalyst is similar in the two reactors.

## A. The CSTR studies of Co(10)/B(x)/TiO<sub>2</sub> Fischer-Tropsch catalysts

### 1. Reaction system

A 1-liter autoclaver, operated as a continuous stirred tank reactor (CSTR), was used for the slurry FTS reactions. Analysis of the gaseous, liquid, and solid (at room temperature) products was conducted both on and off line using a variety of gas chromatographs.

### 2. Procedure

The catalysts used were 10 wt% Co/TiO<sub>2</sub> and 10 wt% Co/ 0.05% B/TiO<sub>2</sub>, prepared by incipient wetness impregnation. Catalyst (about 15 g) was reduced *ex-situ* with hydrogen at 300°C for 16 h and transferred under the protection of helium to CSTR to mix with 300 g of melted P.W. 3000. The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with a flow rate of 30 NLh<sup>-1</sup>gc<sup>-1</sup> (25°C, 0.1 mPa). The reactor temperature was increased to 280°C at a rate 120°C h<sup>-1</sup> and maintained at this activation condition for 24 h. After the activation period, the reactor temperature was decreased to 210°C and synthesis gas was then introduced. During the entire run the reactor temperature was 230°C, the pressure was 350 psig, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was varied from 1 to 5 NL h<sup>-1</sup> gc<sup>-1</sup> at a constant H<sub>2</sub>/CO ratio of 2. Afterwards, the H<sub>2</sub>/CO ratio synthesis gas was varied from 2 to 5 at a constant space velocity of 2 NL h<sup>-1</sup>gc<sup>-1</sup>. The conversion of carbon monoxide and hydrogen and the formation of products were measured during a period of 24 h at each condition.

### 3. Results

The attached figures show that synthesis gas conversion, methane selectivity and hydrocarbon production rate varied with space velocity and the H<sub>2</sub>/CO ratio for two catalysts.

Synthesis gas conversion for two catalysts is shown in Figure 1. The synthesis gas conversion was found to increase with decreasing space velocity. At the higher space velocity (SV>4), the two catalysts showed very similar synthesis gas conversion; at low space velocity (SV<4), the catalyst with 0.05 % B showed a slightly higher conversion.

Figure 2 shows the hydrocarbon production rate as a function of reciprocal flow rate. For the catalyst with 0.05% B, the hydrocarbon rate increased almost linearly with increasing space velocity. For B-free catalyst, the hydrocarbon rate increased first and then kept a constant of 2.0 g/gcat./h with increasing space velocity; however, the difference between the two runs is small.

From Figure 3, we find the methane fraction of the hydrocarbons increased with increasing space velocity. For all space velocities, the catalyst with 0.05% B showed higher methane selectivity.

For two catalysts, the effects of  $H_2/CO$  ratio on conversion and methane selectivity are very similar (Figures 4 and 5). Increasing the ratio of  $H_2/CO$  resulted in: (i) synthesis gas conversion increased first and then decreased and reached a maximum at the  $H_2/CO$  of 4; (ii) methane selectivity increased almost linearly.

In summary, the presence of boron produced only minor changes on the properties of the cobalt catalyst. In earlier studies, it was shown that the presence of boron made the catalyst less susceptible to poisoning by sulfur.

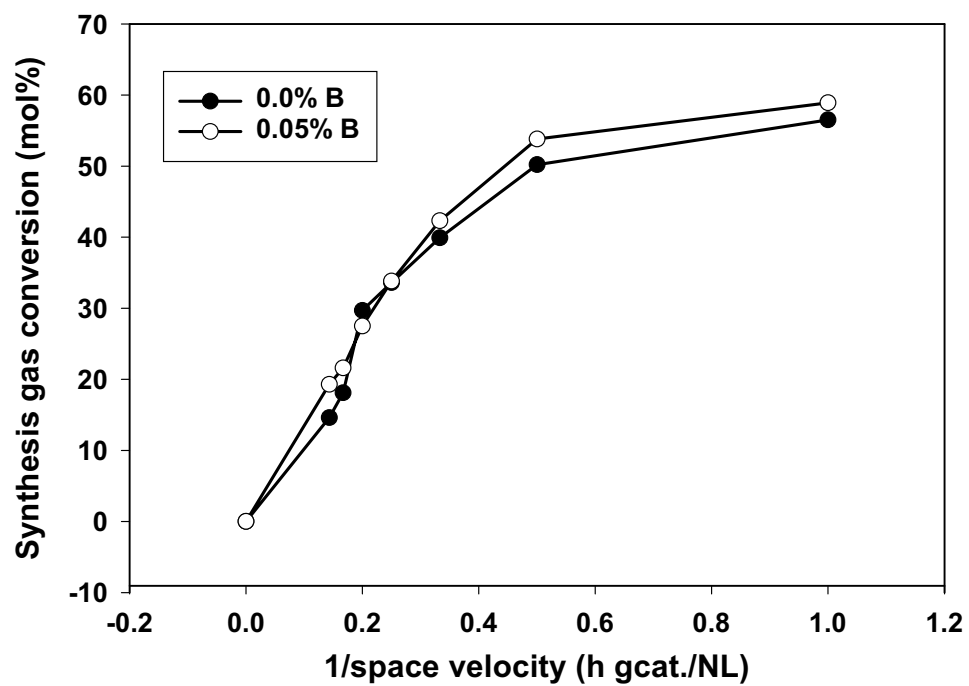


Figure 1. Synthesis gas conversion as a function of reciprocal flow rate

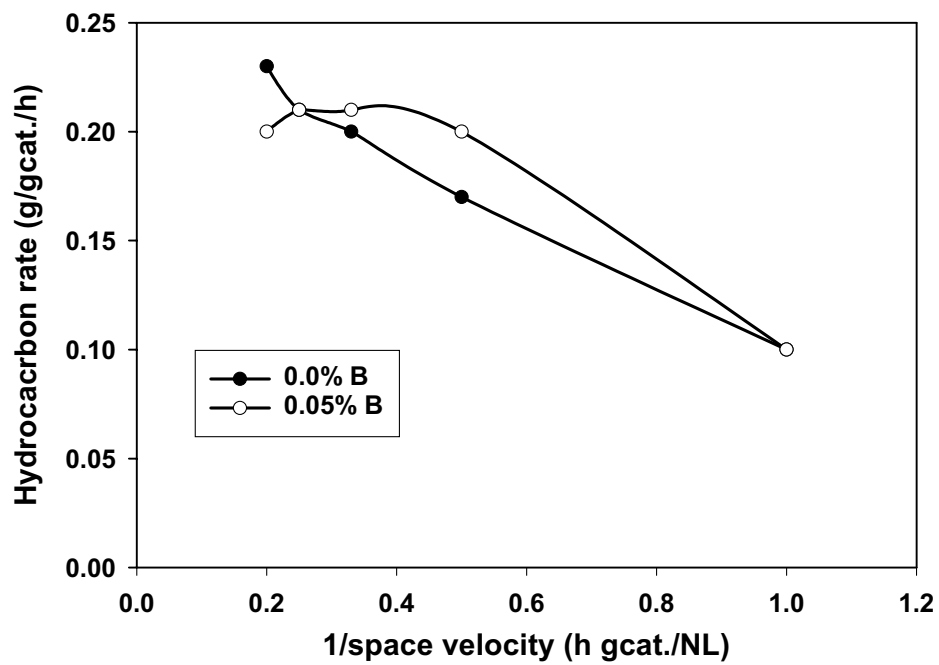


Figure 2. Hydrocarbon production rate as a function of reciprocal flow rate

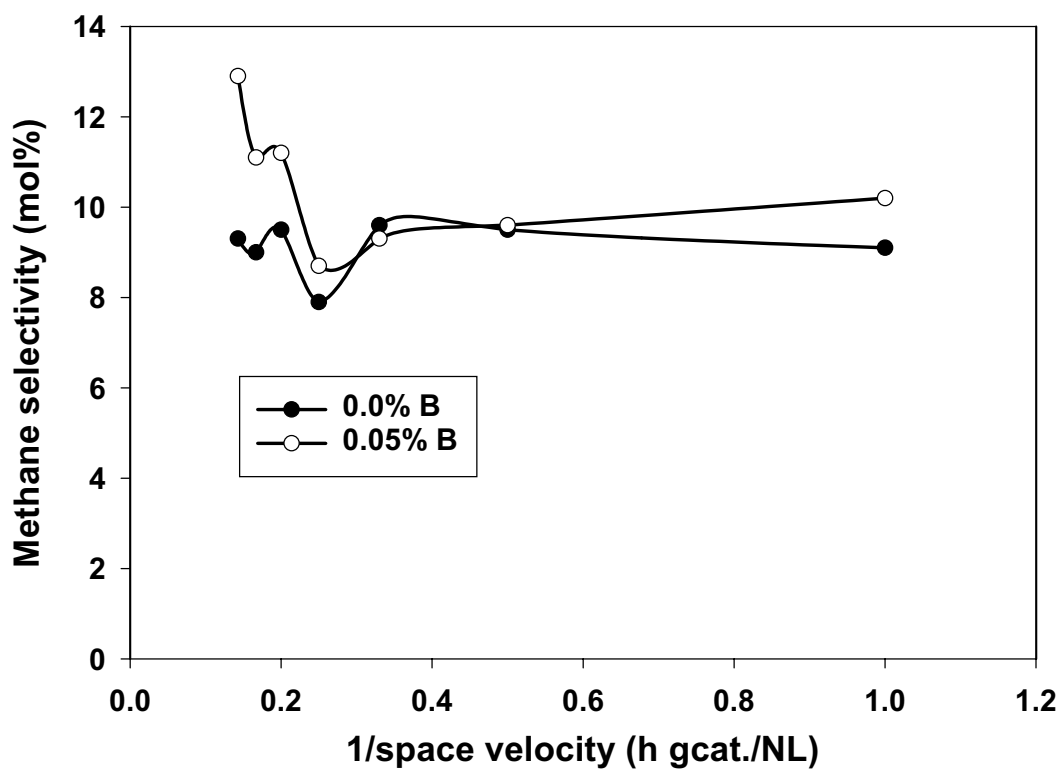
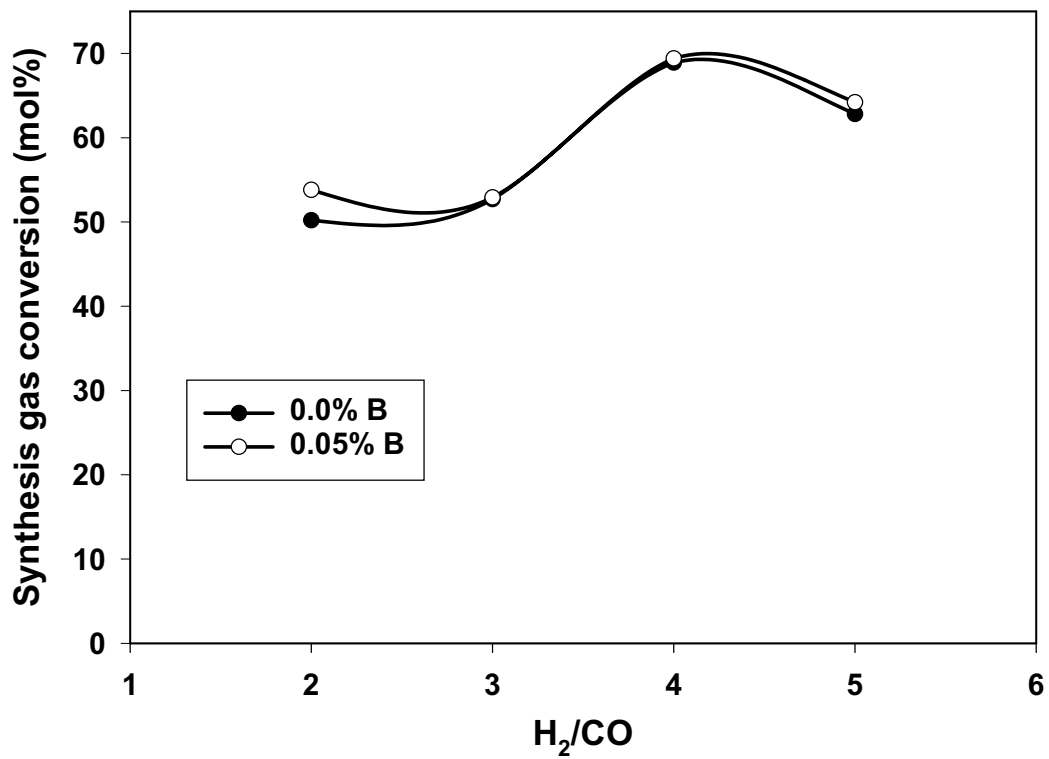
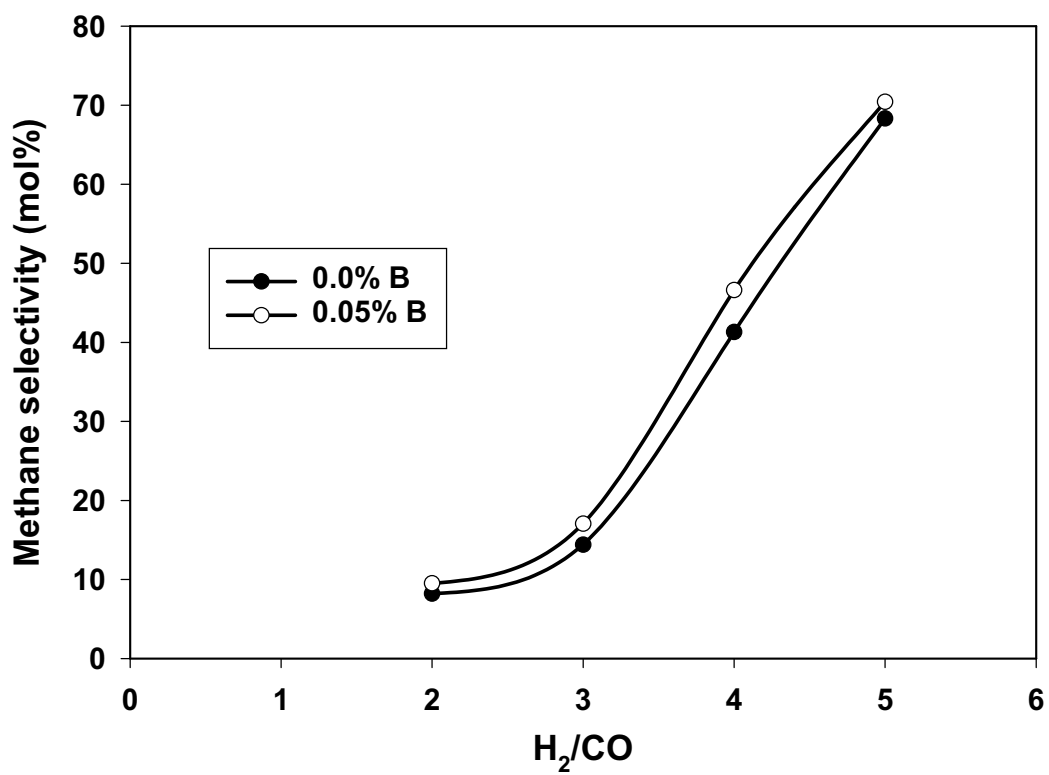


Figure 3. Methane selectivity vs reciprocal flow rate





**Figure 4. Synthesis gas conversion vs ratio of H<sub>2</sub> to CO  
(at SV=2 NL/gcat./h)**



**Figure 5. Methane selectivity vs ratio of H<sub>2</sub> to CO  
(at SV=2 NL/gcat./h)**

## **B. Study of supercritical phase Fischer-Tropsch synthesis**

### **1. Introduction:**

Fischer-Tropsch synthesis has been studied extensively in both gas and liquid phase reaction media, in which fixed-bed and CSTR or bubble column slurry phase reactors were used respectively. Gas phase reactions may exhibit higher initial reaction rates but also is inevitably accompanied by local overheating of the catalyst surfaces as well as by the deposition of heavy wax in catalyst pores. Local overheating of the catalyst and the plugging of the pores of the catalyst may lead to deactivation of the catalyst and also to an increase in methane selectivity. Liquid phase reactions have superior heat removal capabilities when compared to gas phase reactions and are, therefore, able to maintain a relatively constant reaction temperature throughout the whole reactor. Another advantage of liquid phase synthesis is that the high molecular weight products are more soluble in the liquid media compared to gas phase reaction media. However, the diffusion of synthesis gas into the pores of the catalysts may be slower in the slurry phase so that the overall reaction rate may therefore be lower. In addition, problems may arise as the accumulation of high molecular weight products in the reactor during the operation, and the *in situ* separation of fine catalyst particles from the heavy products remain to be solved for liquid phase reaction. The ideal FT synthesis medium would therefore be one with gas-like transport properties and liquid like heat capacity and solubility characteristics. Such a desired combination of fluid properties can possibly be obtained by conducting the Fischer-Tropsch synthesis in a supercritical reaction media.

The critical temperature of a fluid is the highest temperature at which liquid and vapor can exist together. The pressure at which condensation of vapor to liquid occurs when the temperature is equal to the critical temperature is the critical pressure. At temperatures above the critical temperature a fluid cannot undergo a transition to a liquid phase, regardless of the pressure applied. A fluid is said to be supercritical when its temperature and pressure exceed the temperature and pressure at the critical point. Supercritical fluid (SCF) are attractive media for chemical reactions because of their unique properties such as viscosity, diffusivity, density and

solubility. Many of the physical and transport properties of an SCF are intermediate between those of a liquid or a gas. Changing the pressure near the critical region can tune the density and transport properties of a fluid to obtain unique fluid properties (e.g., gas-like transport properties or liquid-like solvent power), which offer certain advantages in heterogenous catalysis reactions. Specific to the Fischer-Tropsch synthesis reaction, it seems SCF can possibly in situ extract the heavy hydrocarbons from the catalyst pores, thereby extending catalyst lifetime. The diffusion of reactant, hydrogen and carbon monoxide, as well as both primary and secondary hydrocarbon products could also be effected by SCF and favorably affect reaction rate and selectivity.

Studies on Fischer-Tropsch synthesis in supercritical media have, to date, been done primarily by three groups of scientists. Fujimoto's group is a pioneer in the area, an excellent job was done by applying the idea to Fischer-Tropsch synthesis; however, the lack of steady-state data made the results less convincing than desired. Bukur's group did steady state work; nevertheless, by using propane as the supercritical media, the density of the solvent is not high enough to attain the optimum solubility properties. Subramaniam's group did the pressure tuning work using hexane as the solvent; still, different syngas partial pressures and residence times were used to compare the activity and selectivity. Therefore, too many variables were introduced to draw solid conclusions.

Steady-state supercritical Fischer-Tropsch synthesis was studied in our work using a fixed-bed reactor and an unpromoted Co/SiO<sub>2</sub> catalyst. This serves as the baseline for promoted catalyst studies. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain a valid comparison of the impact of solvent density in the catalytic activity and selectivity. Three different partial pressures of the mixture were chosen based on the density-pressure curve in order to investigate the pressure tuning effect to Fischer-Tropsch synthesis near critical region.

## **2. Experimental**

Catalyst preparation: A 2kg batch of 15% Co/SiO<sub>2</sub> catalyst was prepared by incipient wetness impregnation method using Davisil 644 Silica gel as support (surface area 300m<sup>2</sup>/g, pore

volume: 1.15 cm<sup>3</sup>/g, particle size 100-200 mesh) and an aqueous cobalt nitrate solution for impregnation. The catalyst was dried by being suspended in air at 80°C in a fluidized vessel and then calcined at 400°C for 4 hrs.

Reactor diagram: A schematic of the reactor Figure 1 is the diagram used to do supercritical Fisher-Tropsch study is shown in Figure 1. Basically, it is a plug-flow reactor with a pump for adding the supercritical solvent. A characteristic of the unit is the capability of being able to be repressurized quickly after taking a liquid product for each mass balance period. Since we pump in a significant amount of solvent during the period, its removal as a liquid causes a remarkable pressure drop. The other difference between the reactor and a traditional plug-flow reactor is that we use a three heating zone furnace and the first zone filled with micro-glass beads to vaporize the solvent. We also set up two parallel sets of hot and cold traps to use for mass balance period and period between mass balance to improve the operation.

Pretreatment condition: The catalyst was reduced with mixture of hydrogen and argon. The temperature was increased to 100°C during 30 min and held at 100°C for 30 min, and after that the temperature was increased to 350°C with a rate of 1°C/min, then held at 350°C for 15 hrs.

**Reaction conditions:**

Conditions	P <sub>overall</sub> (MPa)	P <sub>syngas</sub> (Mpa) H <sub>2</sub> :CO =2.0	P <sub>solvent</sub> +P <sub>He</sub> (MPa)	T(°C)	Total Flow Rate (ml/min)	Syngas Flow Rate (ml/min)	He Flow Rate (ml/min)	Solvent Flow Rate* (ml/min)
1	8.0	2.0	6.0	220	200	50	150	0
2	8.0	2.0	6.0	220	200	50	100	50
3	8.0	2.0	6.0	220	200	50	62.5	87.5
4	8.0	2.0	6.0	220	200	50	0	150

\*gas phase flow rate

### 3. Results and discussion:

Physical and transport properties of certain fluids change dramatically with pressure in a range around the critical pressure and at temperatures slightly higher than the critical temperature. They can be made either more gas-like or liquid-like by tuning the pressure. As to Fischer-Tropsch synthesis, the ideal situation is to find a condition where the maximum extraction of hydrocarbon products from catalyst pores can be reached to increase catalyst lifetime. However, diffusivity and viscosity of the fluid can have an impact on the degree of secondary reactions that take place on the surface of catalyst and therefore lead to changes in selectivity. Thus, different solvent and pressure tuning effects of the solvent are important to supercritical Fischer-Tropsch synthesis study.

A near optimal temperature for the cobalt catalyst being used in this study is about 220<sup>0</sup>C; therefore, the critical temperature of the solvent chosen should be below 220<sup>0</sup>C. Since the critical temperature for n-pentane is 197<sup>0</sup>C and for n-hexane is 232<sup>0</sup>C, a mixture of these two solvent can be used to obtain the maximum density. Figure 2 shows a curve of the critical temperature of pentane and hexane mixtures versus the hexane volume percentage. From Figure 2, it is calculated that 55%(V) of hexane/45%(V) of pentane mixture has the highest density whose critical temperature is under 220<sup>0</sup>C.

In order to obtain good representative pressure points to study the tuning effect, it is necessary to have an idea of how density changes with pressure near the critical region. Figure 3 is the density of 55%(V) n-hexane and 45%(V) n-pentane mixture versus pressure curve between 1-15MPa at 220<sup>0</sup>C (a Hysys 2.1 process simulator was used to calculate the density data). Partial pressures of 2.0MPa, 3.5MPa and 6.0MPa of the mixture were chosen to represent the gas-like, supercritical and liquid like conditions, respectively. Helium was used as a balancing gas to keep the overall pressure and residence time constant. Altogether, four conditions were studied; this included no added solvent and three different solvent partial pressures. After taking a liquid sample, helium was charged to the cold trap to make up the pressure drop. Hot and cold traps

temperatures were controlled at 160°C and 0°C respectively. Mass balance time of each sample was around 2 hrs.

Exit flow rate and molar percentage of the components of the gas was used to calculate CO conversion. Normalized exit flow rate was obtained by converting for the increase of flow rate caused by condensation of solvent in the cold trap and the amount of solvent in the exit gas phase. The rate of volume decrease of the reactor-collector may increase rapidly enough for this correction to make a large change in the measured conversion.

CO conversion versus time on stream data are shown in Figure 4. It can be concluded from Figure 4 that the supercritical phase Fischer-Tropsch synthesis significantly alters the total conversion and inhibit the deactivation of the catalyst. As a matter of fact, introducing only 2.0MPa of the pentane-hexane mixture to the reactor increased the CO conversion from 27% to 46%. The mixture at this pressure is not at its supercritical state; however, the density of the reaction media is much higher than condition 1 in which only helium was the balancing gas. Therefore, the solubility of the hydrocarbon in reaction media was increased, and it is concluded that the catalyst pores contained less liquid and more active sites were available which leads to the increase of the CO conversion. After 3.5MPa of pentane-hexane mixture was fed into the reactor (condition 3), the reaction media should be in the supercritical phase. The density is much higher than that in condition 2, causing the solubility to increase significantly, while, the diffusivity of reactant and the product is reasonably fast; therefore, the highest CO conversion was obtained. When the partial pressure of pentane-hexane mixture reached 6.0MPa (condition 4), the density of the mixture is more liquid-like and the maximum extraction of the heavy wax product occurs; however, the diffusivity of the media is also more liquid like. This may have limited the Fischer-Tropsch reaction and hence slightly lower CO conversion was observed. Several steady-state data were obtained for each condition and the reproducibility is good as shown by the data in Figure 4 for repeating the measurements at each condition. Throughout the period that solvent was introduced into the reactor, the deactivation is rather negligible. After switching back to the condition 1 in which no solvent was introduced, the CO conversion

decreased to 40% from 49% at condition 2. The deactivation was rapid at this condition and conversion decreased to 16.0% in only 33 hrs.

Since the analysis of the liquid product is not complete, the  $\alpha$  value of the reaction has not been defined. Nevertheless, the selectivities of methane and CO<sub>2</sub> were calculated and the results are interesting. Figures 5 and 6 show the selectivity of methane and carbon dioxide with time on stream, respectively. It can be seen that methane selectivity decreased dramatically with the introduction of solvent into the reactor system. The higher the partial pressure of the pentane-hexane mixture, the lower the methane selectivity. The formation of CO<sub>2</sub>, while small, and parallel that of methane.

#### **4. Conclusion**

Steady-state supercritical Fischer-Tropsch synthesis was studied using a fixed-bed reactor and a Co/SiO<sub>2</sub> catalyst. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain valid comparisons.

Three different partial pressure points of the mixture were chosen based on the density-pressure curve to investigate the pressure tuning effect for Fischer-Tropsch synthesis near critical region. It was found that supercritical phase Fischer-Tropsch synthesis can significantly inhibit the deactivation of catalyst, presumably due to the extraction of heavy hydrocarbon products from catalyst pores and possibly improving the heat transfer in plug-flow reactor. The highest CO conversion was obtained when the solvent partial pressure is just above its critical pressure compared to its more gas-like or liquid-like state. Reproducible data were obtained by repeating the measurements.

Methane and carbon dioxide selectivity decreased dramatically with an increase of pentane-hexane partial pressure. The selectivity of reaction and  $\alpha$  value of different conditions will be defined in future work.



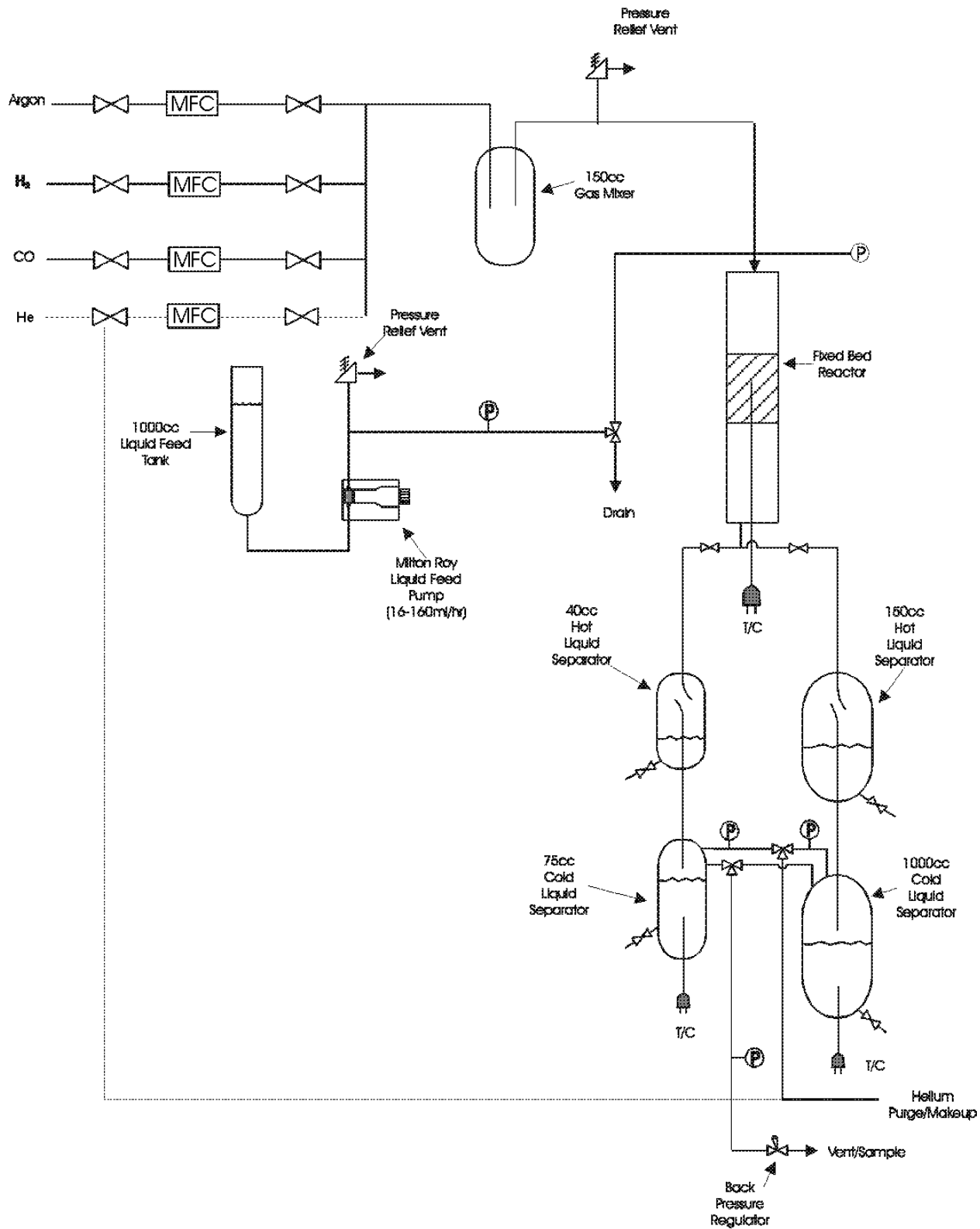


Figure 1. Supercritical FT Reactor-Flow Diagram

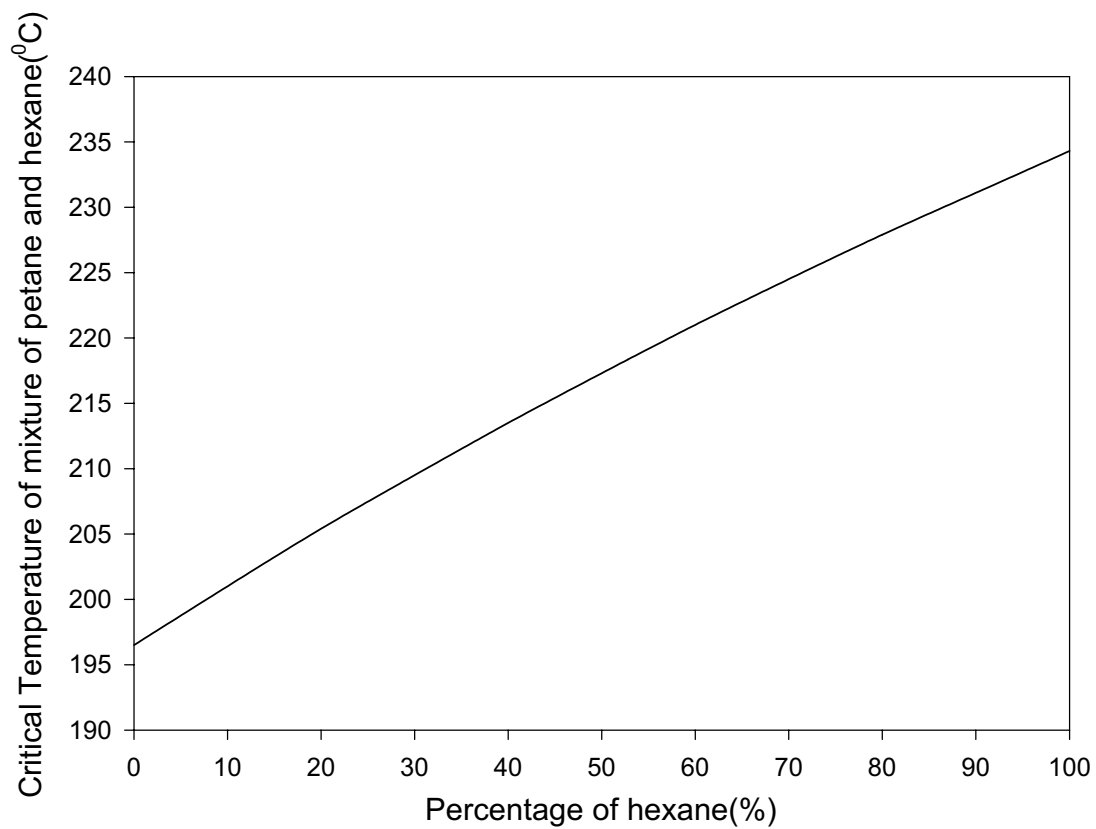


Figure 2. Critical temperature of pentane and hexane mixture with hexane percentage.

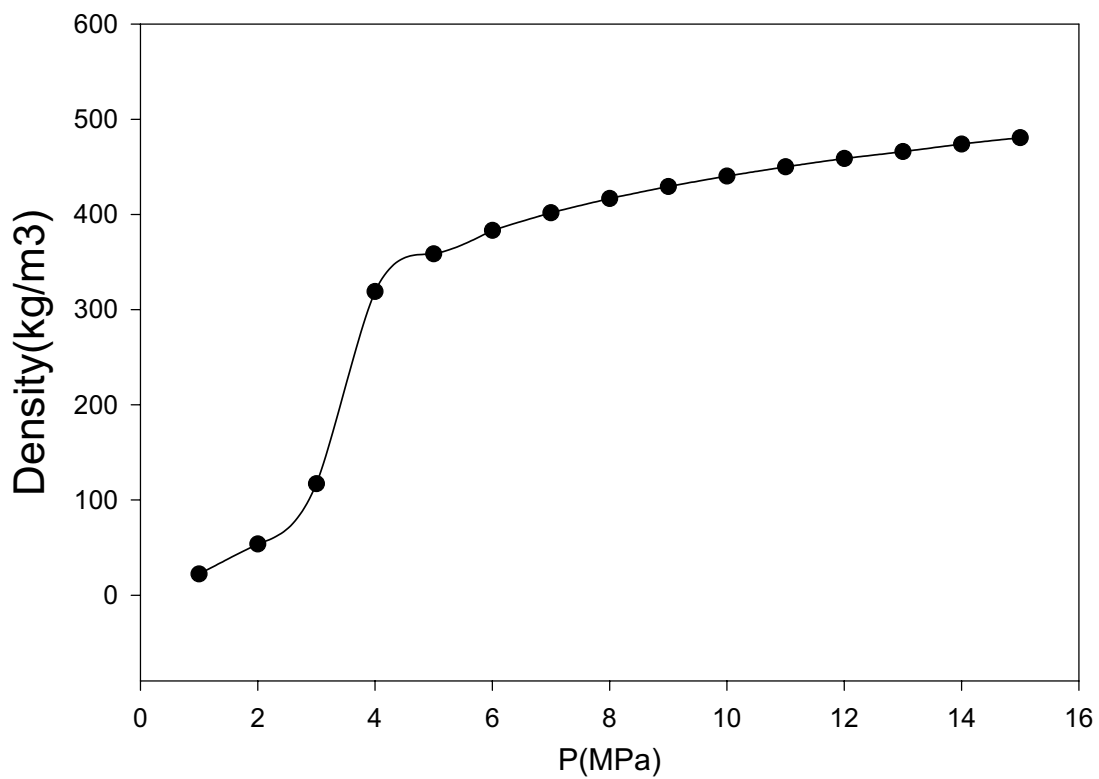


Figure 3. Density vs. pressure mixture of 55%(V) pentane and 45%(V) hexane.

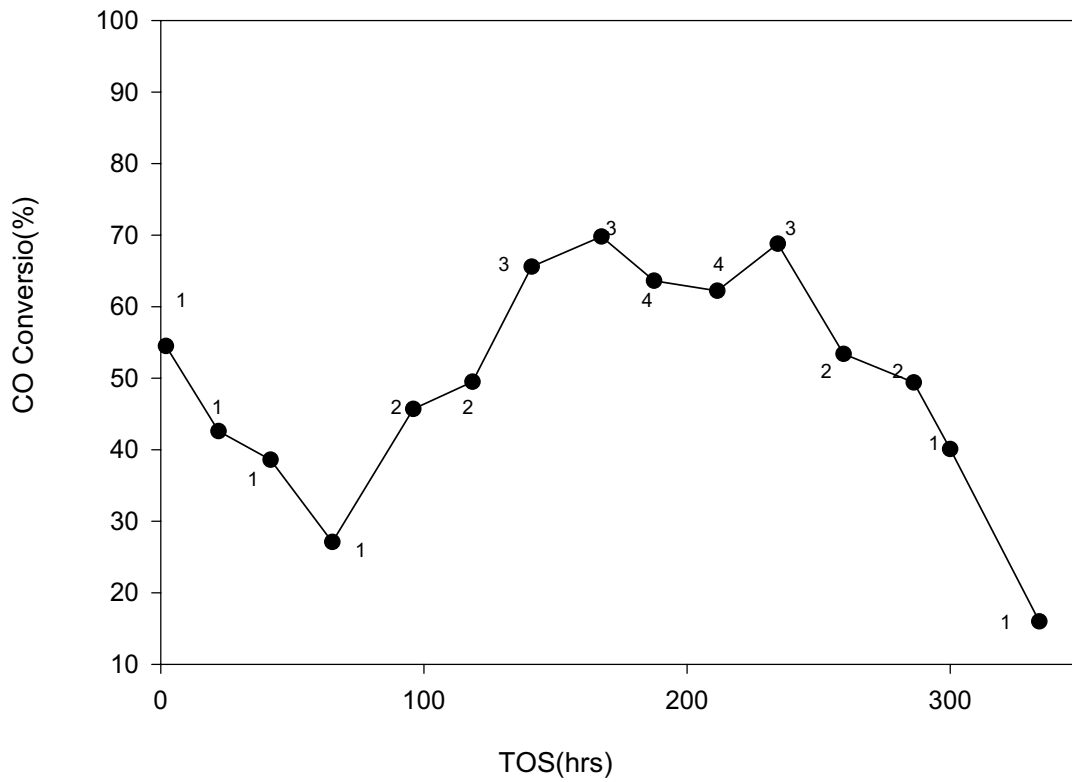


Figure 4. Run YQZ 304. CO conversion vs. TOS ( $T = 220^{\circ}\text{C}$ ,  $P_{\text{total}} = 8.0 \text{ mpa}$ ,  $P_{\text{syngas}} = 2.0 \text{ mpa}$ ,  $\text{H}_2:\text{CO} = 2:1$ ; 1 =  $P_{\text{He}} = 6.0$ ,  $P_{\text{C5+C6}} = 0$ ; 2 =  $P_{\text{He}} = 4.0$ ,  $P_{\text{C5+C6}} = 2.0$ ; 3 =  $P_{\text{He}} = 2.5$ ,  $P_{\text{C5+C6}} = 3.5$ ; 4 =  $P_{\text{He}} = 0$ ,  $P_{\text{C5+C6}} = 6.0$ ).

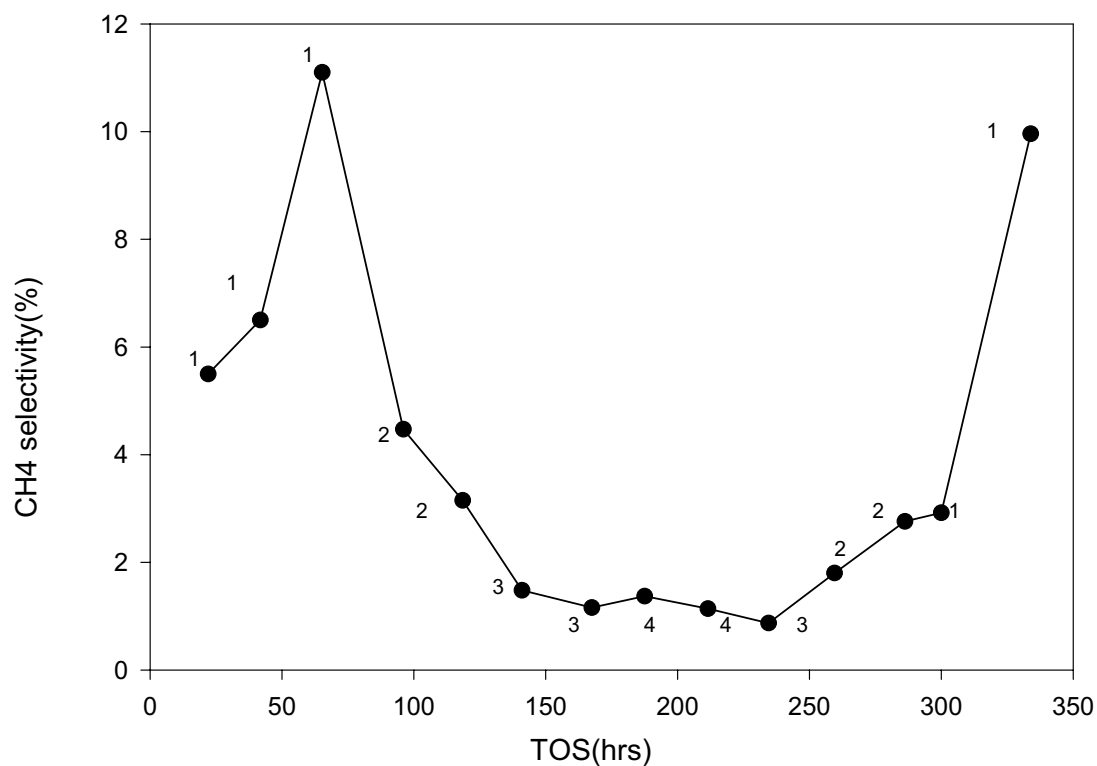


Figure 5. Run YQZ 304. CH<sub>4</sub> selectivity vs. TOS (T = 220°C, P<sub>total</sub> = 8.0 mpa, P<sub>syngas</sub> = 2.0 mpa, H<sub>2</sub>:CO = 2:1; 1 = P<sub>He</sub> = 6.0, P<sub>C5+C6</sub> = 0; 2 = P<sub>He</sub> = 4.0, P<sub>C5+C6</sub> = 2.0; 3 = P<sub>He</sub> = 2.5, P<sub>C5+C6</sub> = 3.5; 4 = P<sub>He</sub> = 0, P<sub>C5+C6</sub> = 6.0).

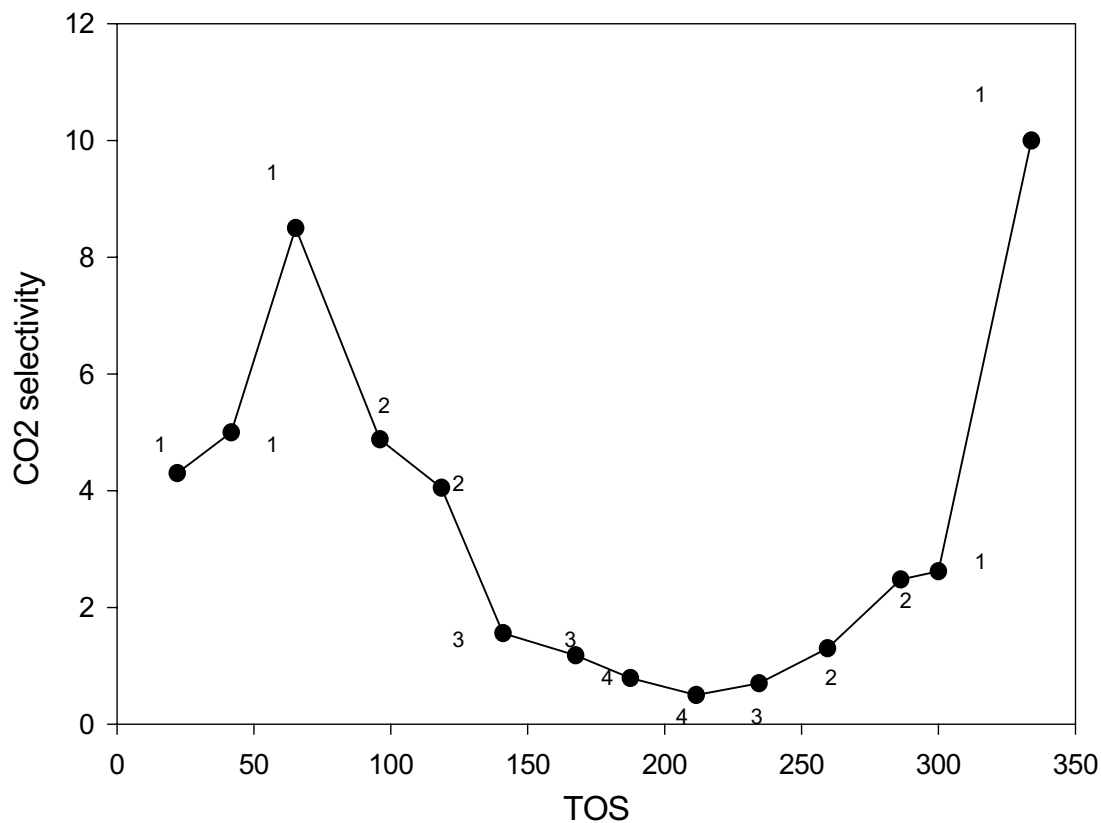


Figure 6. Run YQZ 304. CO<sub>2</sub> selectivity vs. TOS (T = 220°C, P<sub>total</sub> = 8.0 mpa, P<sub>syngas</sub> = 2.0 mpa, H<sub>2</sub>:CO = 2:1; 1 = P<sub>He</sub> = 6.0, P<sub>C5+C6</sub> = 0; 2 = P<sub>He</sub> = 4.0, P<sub>C5+C6</sub> = 2.0; 3 = P<sub>He</sub> = 2.5, P<sub>C5+C6</sub> = 3.5; 4 = P<sub>He</sub> = 0, P<sub>C5+C6</sub> = 6.0).

**Task 9. Cobalt Catalyst Life Testing**

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled for further activity to report.

**Task 10. Cobalt Catalyst Mechanism Study**

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled or further activity to report.

**Task 11. University of California, Berkeley (Subcontract)**

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H<sub>2</sub> on multi-component catalysts based on Fe as the active component.