

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 Task 7 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. Comparison of Fischer-Tropsch synthesis in conventional fixed bed, CSTR and supercritical reactors on unpromoted cobalt catalyst

Introduction

Fischer-Tropsch synthesis has been studied in different reactor systems. Plug flow reactor, continuous stirring tank reactor and fluidized bed reactor have been used. Gas, liquid and supercritical reaction media were used in different reactor systems and under different operating conditions. Fischer-Tropsch synthesis reaction performed in the supercritical phase offers the opportunity to improve the heat transfer property and the ability to extract the heavy wax product from catalyst pores, and therefore extends catalyst lifetime. However, the introduction of the supercritical solvent into the reactor system would increase the operation cost not only because of the consumption of the solvent but also because of the much higher operating pressure. The continuously stirring tank reactor, on the other hand, is another alternative to the rapid catalyst deactivation in plug flow reactor. The heat transfer property is even better than the supercritical media; the disadvantage is that diffusion is slower in the slurry phase than plug flow reactor and therefore the overall reaction rate would be lower. The study conducted on supercritical Fischer-Tropsch synthesis using an unpromoted Co/SiO₂ catalyst prepared in this lab indicated that the lower rate of catalyst deactivation did occur; however, the selectivity of methane decreased by the application of the supercritical solvent. The same catalyst was studied in the continuously stirring tank reactor to compare the activity, selectivity, deactivation rate etc.

Experimental

A 2kg batch Co/SiO₂ catalyst was prepared using an incipient wetness impregnation technique. The support material is Davisil silica 644 (surface area 300m²/g; pore volume: 1.15cm³/g) and the cobalt loading is 15%. The CSTR reactor was loaded with 17.7g of the catalyst. The initial conditions for the reaction were 350psig, 220°C, with the trap temperatures at 200, 130 and 0°C. The feed gas was initially set to 16.03 slph with a percentage composition of 10.73 H₂, 5.03 CO for a H₂:CO ratio of 2.02 and 6.04 WHSV. 300 Grams of startup oil PW3000 was used. The catalyst was pretreated in a fixed bed reactor under hydrogen at 350°C for 15hrs and then added to the startup oil without exposure to the atmosphere.

Results and discussion

Figure 1 shows the change of CO conversion with time on stream in the CSTR at a space velocity of 1.0 sl/g/hr. It shows that, except for the rapid decline of CO conversion in the first 24 hrs of time on stream, the catalyst deactivated at a fairly stable rate of 1.6% CO conversion per day. Figure 2 is the CO conversion curve for the fixed bed and supercritical Fischer-Tropsch synthesis over the same catalyst at the same syngas partial pressure, same temperature and under the same space velocity. The deactivation rate for the fixed-bed operation before using the supercritical solvent is about 9.9%CO conversion per day which is much faster than in the CSTR. The addition of the supercritical solvent into the reactor, on the other hand, decreases the deactivation rate of the catalyst significantly, as one can see from Figure 2. The methane selectivity vs time on stream curves of the CSTR and fixed bed reactors are described in Figures 3 and 4. Similar methane selectivity was obtained at the same level of CO conversion for the fixed-bed reactor and the CSTR. Nevertheless, the methane selectivity for the supercritical Fischer-Tropsch synthesis is much lower than in both conventional fixed-bed and CSTR. The

same trend can be observed for the CO₂ selectivity under these three conditions (Figures 5 and 6).

At the same space velocity, the hydrocarbon productivity rate of the catalyst in the conventional fixed-bed reactor, CSTR and supercritical Fischer-Tropsch synthesis are 0.50, 0.59 and 0.85 (under the most favorable condition), respectively. Therefore, the supercritical Fischer-Tropsch synthesis is still a promising alternative route compared to the conventional fixed-bed synthesis. However, the CSTR is also proved to have a lower catalyst deactivation rate. The choice between CSTR and supercritical reactor depends on the comparison between productivity and the investment and operation cost.

The activity and selectivity of the catalyst were tested in a CSTR at different space velocities, and the CO conversion vs 1/GHSV curve was plotted in Figure 7. It is concluded that the CO conversion changes linearly with the reciprocal of space velocity at the conversion range being studied.

Figure 8 shows the hydrocarbon productivity rate vs the reciprocal of space velocity. One can draw the conclusion that the productivity does not change over the space velocity range being studied. It again supports the idea that at low CO conversion range, Fischer-Tropsch synthesis rate on unpromoted cobalt catalyst in a CSTR is independent of CO concentration, provided the H₂/CO ratio remains constant.

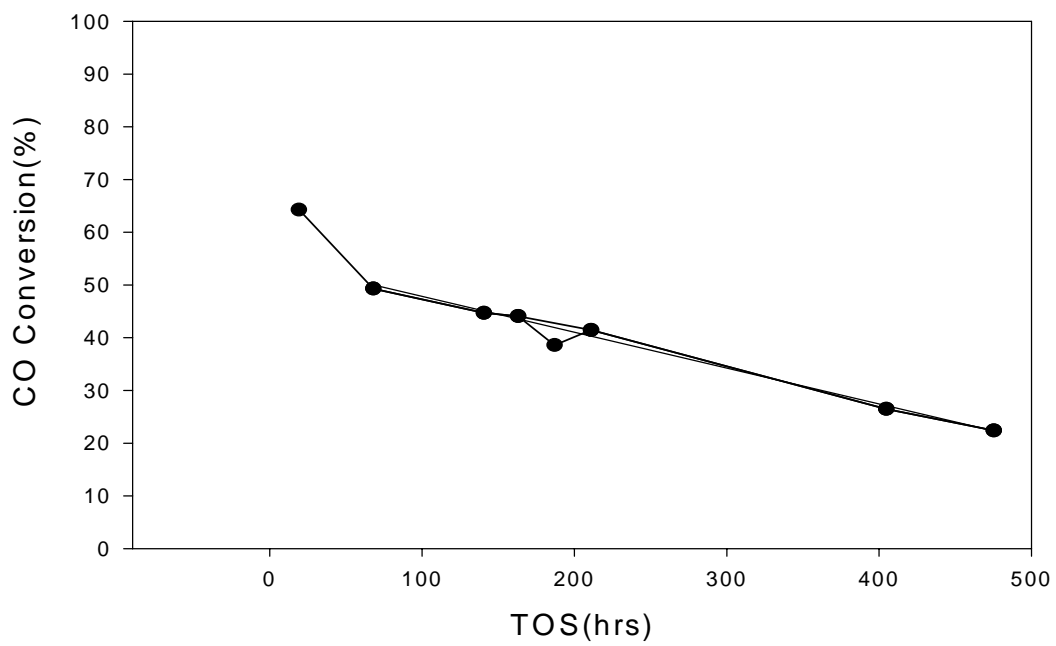


Figure 1. CO conversion vs time on stream in CSTR
(T = 220°C, GHSV = 1.0 SL/hr/g catalyst, P = 295 psig).

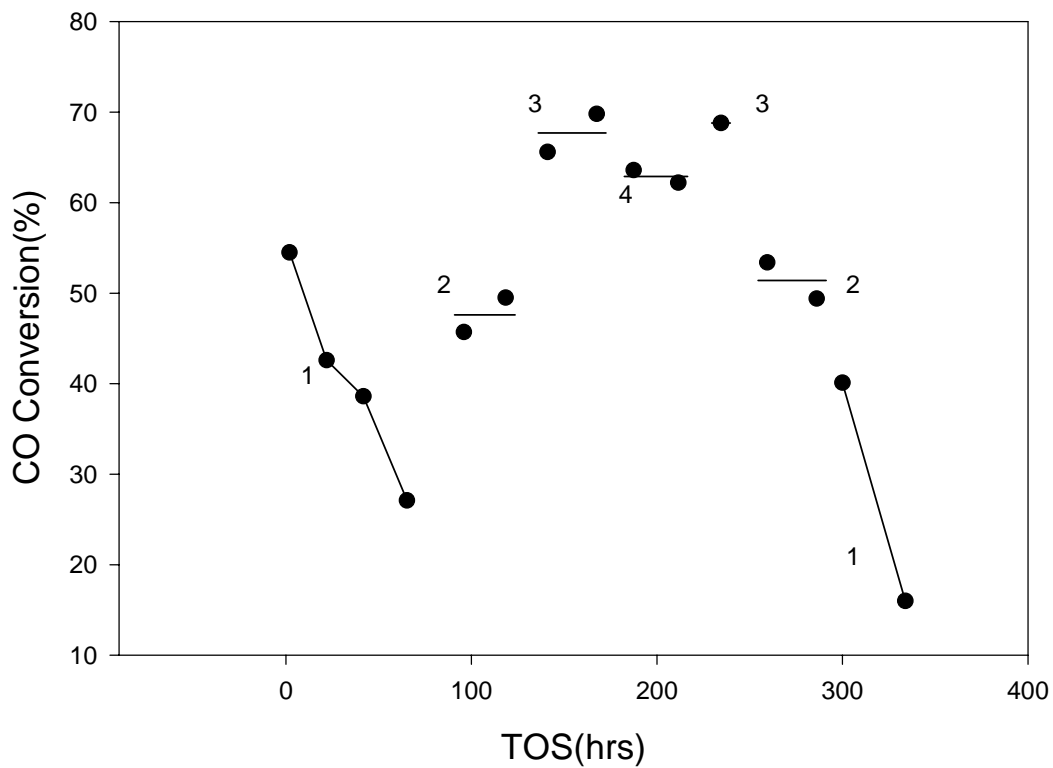


Figure 2. CO Conversion vs. time on stream ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$, (1) $P_{\text{He}}=6.0\text{ MPa}$, $P_{\text{C5+C6}}=0$; (2) $P_{\text{He}}=4.0\text{ MPa}$, $P_{\text{C5+C6}}=2.0\text{ MPa}$; (3) $P_{\text{He}}=2.5\text{ MPa}$, $P_{\text{C5+C6}}=3.5\text{ MPa}$; (4) $P_{\text{He}}=0$, $P_{\text{C5+C6}}=6.0\text{ MPa}$).

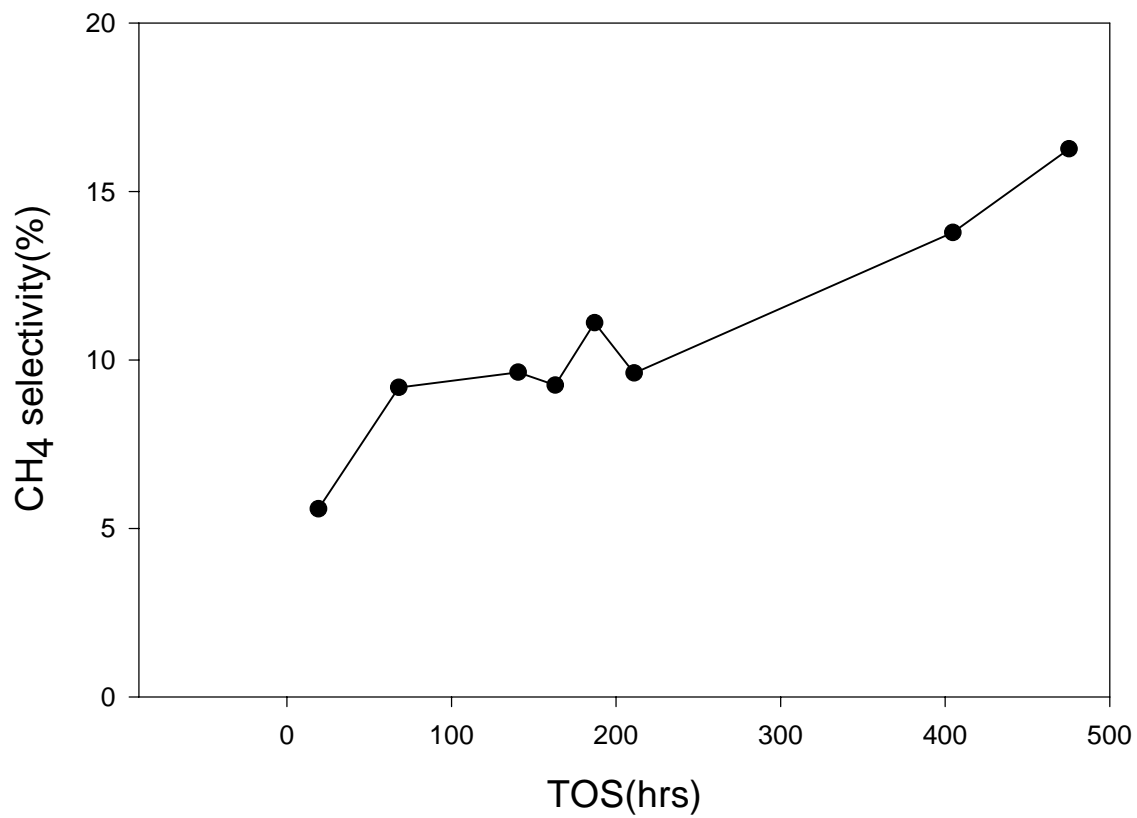


Figure 3. CH₄ selectivity vs time on stream in CSTR
(T = 220°C, P = 295 psig, GHSV = 1.0 SL/hr/g-catalyst).

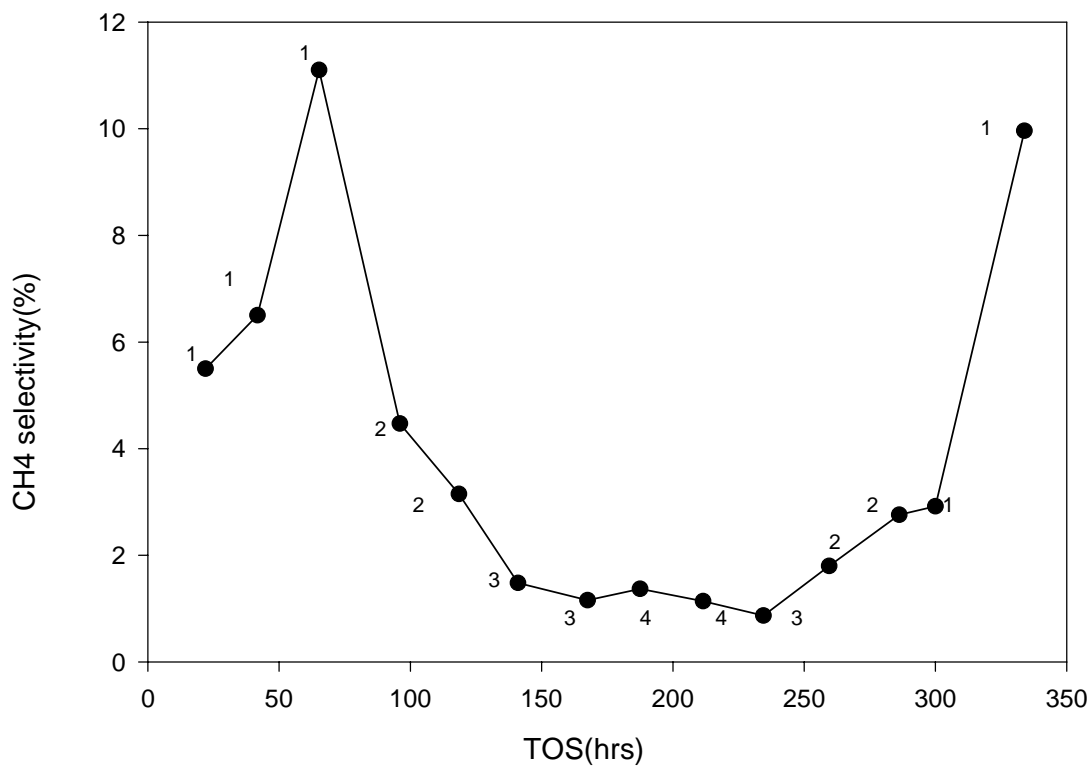


Figure 4. CH₄ selectivity vs time on stream in fixed bed and supercritical reactors ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$. (1) $P_{\text{He}}=6.0$, $P_{\text{C}_5+\text{C}_6}=0$; (2) $P_{\text{He}}=4.0$, $P_{\text{C}_5+\text{C}_6}=2.0$; (3) $P_{\text{He}}=2.5$, $P_{\text{C}_5+\text{C}_6}=3.5$; (4) $P_{\text{He}}=0$, $P_{\text{C}_5+\text{C}_6}=6.0$).

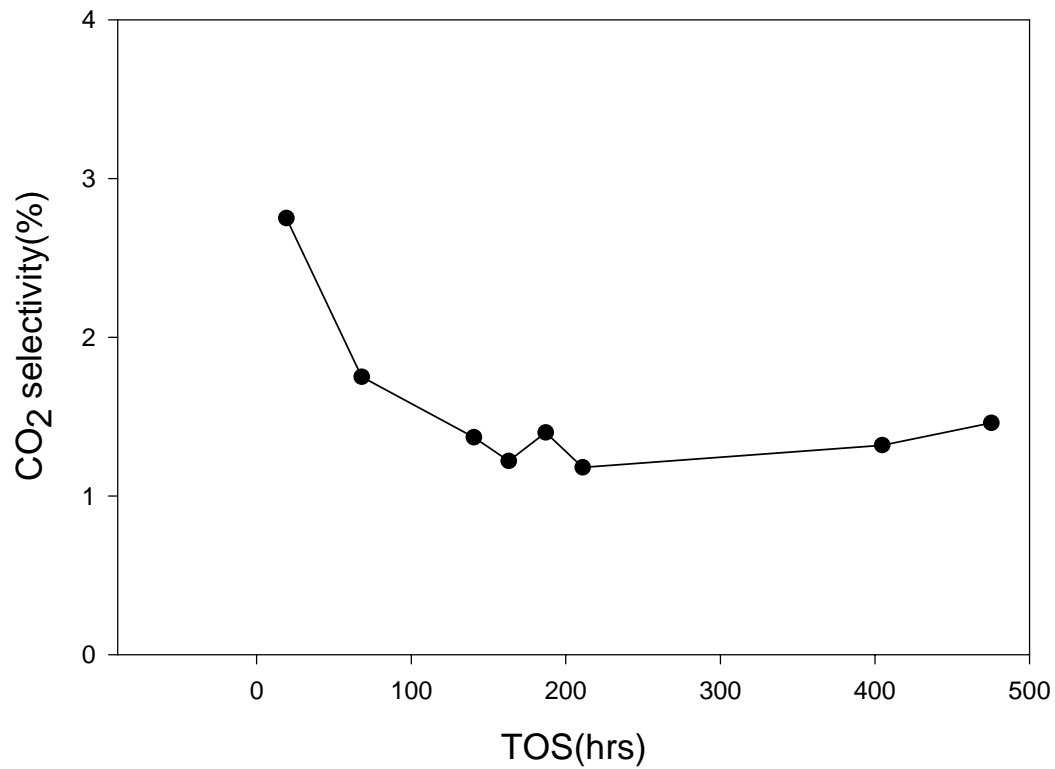


Figure 5. CO₂ selectivity vs time on stream in CSTR (T=220°C, GHSV=1.0 SL/hr/g catalyst, P=295 psig).

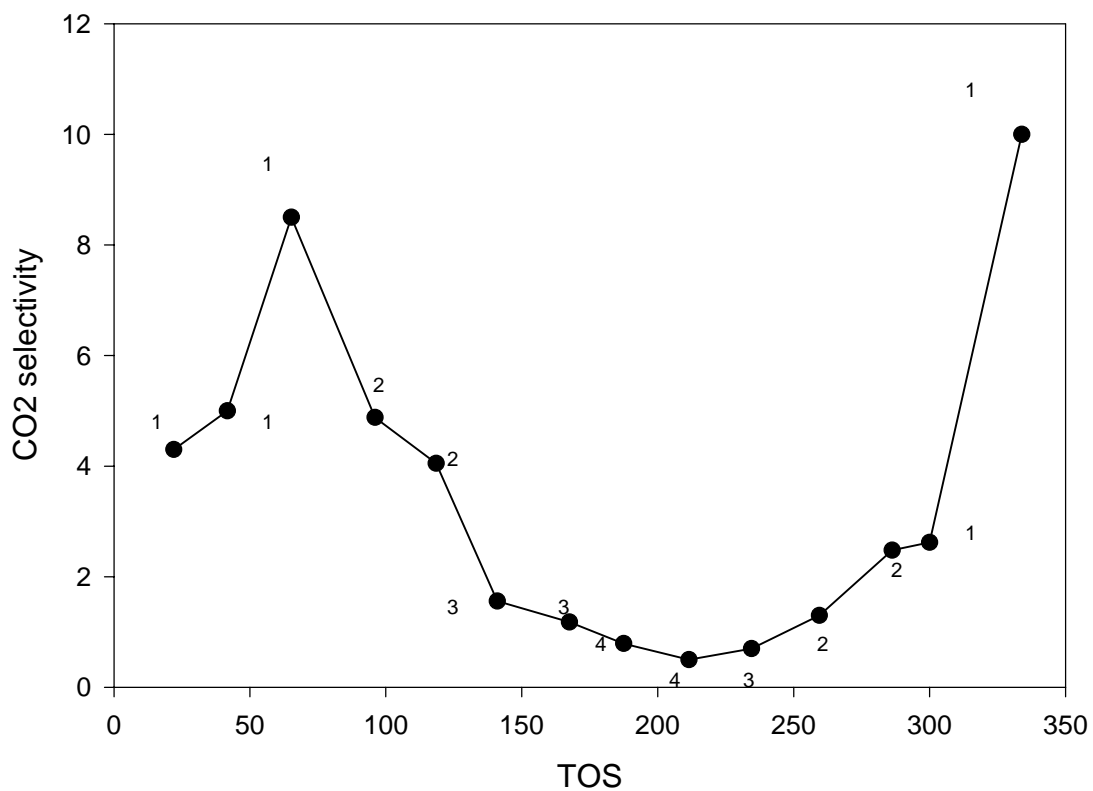


Figure 6. CO₂ selectivity vs time on stream in fixed bed and supercritical reactors (T=220oC, Ptotal=8.0 MPa, P_{syngas}=2.0 MPa, H₂:CO=2:1. (1) P_{He}=6.0, P_{C5+C6}=0; (2) P_{He}=4.0, P_{C5+C6}=2.0; (3) P_{He}=2.5, P_{C5+C6}=3.5; (4) P_{He}=0, P_{C5+C6}=6.0).

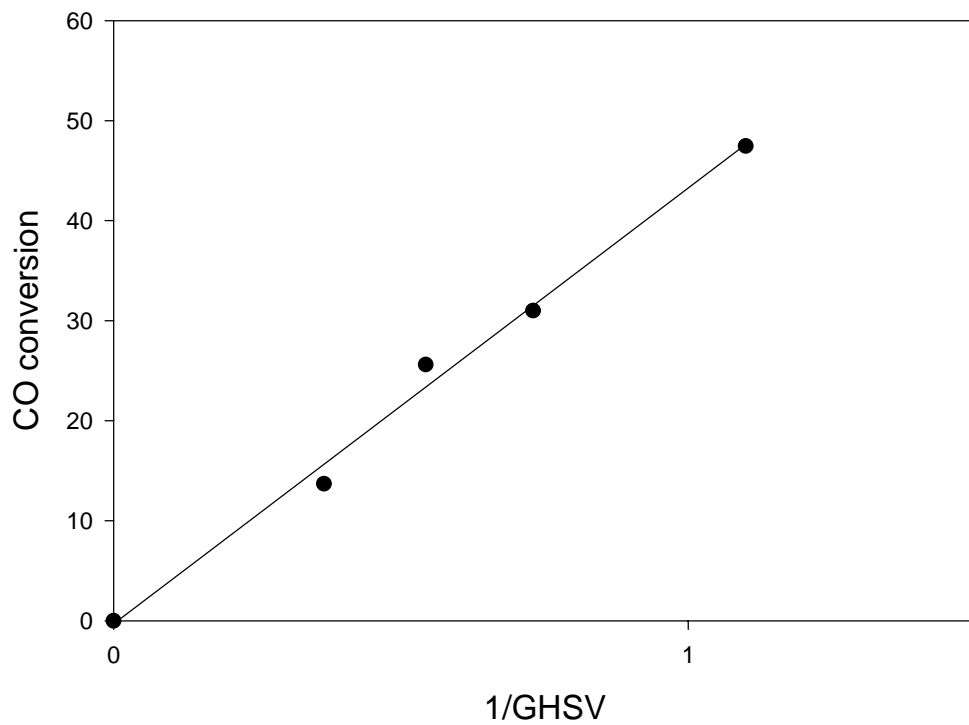


Figure 7. CO conversion vs 1/GHSV at 100hrs time on stream in CSTR (T=220°C, P=295 psig).

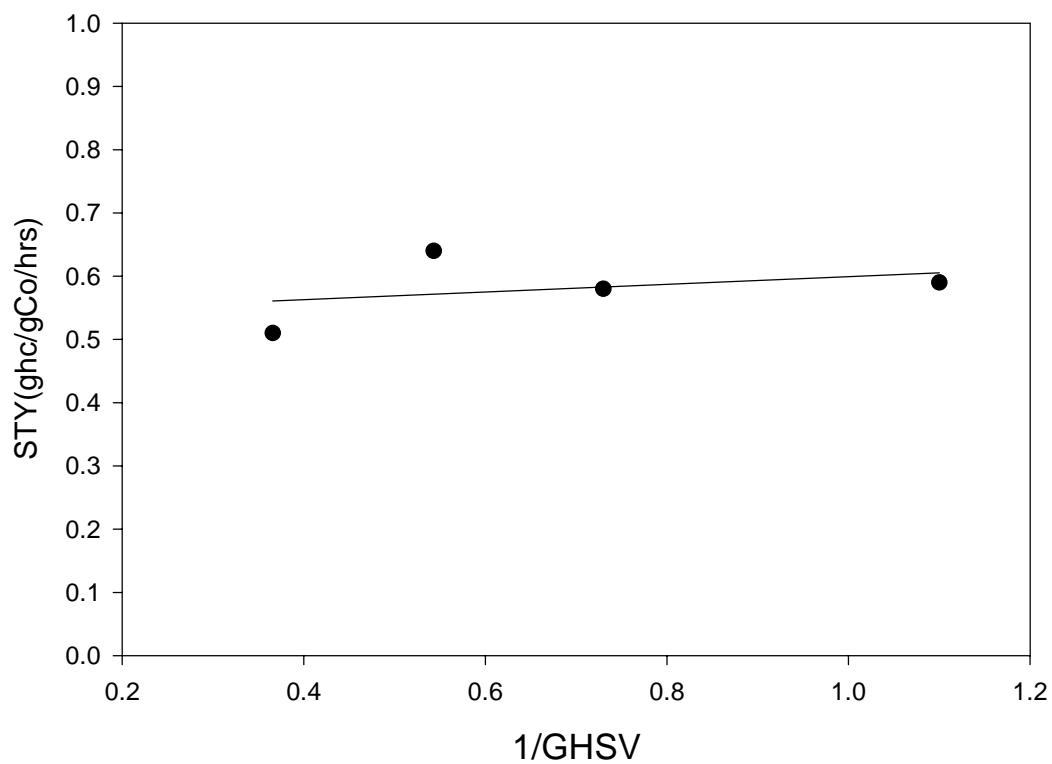


Figure 8. STY vs 1/GHSV in CSTR
(T = 220°C, P = 295 psig).

B. CO and CO₂ Hydrogenation Over Co/SiO₂ Catalyst

Summary

CO and CO₂ hydrogenation was studied in a fixed bed reactor using a Co/SiO₂ catalyst. The reaction was carried out at 220°C, 350psig, H₂:CO=2:1, H₂:CO₂ = 2.1, with a total flow rate of 150 mL/min (3NL/hr/g catalyst) and a H₂+CO, H₂+CO₂ or H₂+CO+CO₂ flow rate of 50 mL/min(1NL/hr/g catalyst). CO, CO₂ and CO,CO₂ mixture feed gas was used, respectively, for comparison. The results indicated that in the presence of CO, CO₂ hydrogenation was very small. For the cases of only CO or only CO₂ hydrogenation, the activity of the two were similar but the selectivity was very different. For CO hydrogenation, normal Fischer-Tropsch synthesis product distributions were observed with an α of about 0.80; in contrast, the CO₂ hydrogenation product contained about 70% methane. Thus, CO₂ and CO hydrogenation appears to follow different reaction pathways.

Introduction

Fixation of carbon dioxide has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse effect. One approach that has attracted attention is to produce synthesis gas through its reaction with methane even though the syngas produced only has a H₂/CO ratio of 1 for the idealized reaction. Another option is to recycle carbon dioxide to a gasification unit; however, there is a limit to the amount of carbon dioxide that can be utilized in this manner. Another approach is to hydrogenate carbon dioxide in Fischer-Tropsch synthesis (FTS) plants; this has become an attractive approach even though one must find a source of hydrogen to accomplish this.

For high temperature (330-350°C) FTS the water-gas-shift (WGS) reaction is sufficiently rapid so that it is nearly at the equilibrium composition. The hydrogenation of CO₂ at high temperatures is possible and occurs in the fluid bed reactors operated by Sasol and Moss gas.

However, the use of a slurry phase bubble column reactor is very attractive since its use allows the FTS reaction to be carried out isothermally. In the liquid phase synthesis, lower temperatures must be utilized (220-240°C) with either a cobalt or iron catalyst. It was of interest to compare the FTS reactions of CO and CO₂ with a cobalt catalyst. In this initial work a simple catalyst formulation has been utilized: cobalt supported on a silica without any promoters.

Experimental

The catalyst was prepared by three incipient wetness impregnations of silica (Davisil 644, 100-200 mesh, 300 m²/g, and pore volume of 1.15 cm³/g) with aqueous cobalt nitrate to produce a final loading of 15 wt.% CO. The material was dried in a fluidized bed and then calcined for 4 hrs. in an air flow at 400°C. Three grams of the calcined catalyst was diluted with 15 g of glass beads and placed in a fixed bed reactor where it was reduced in a H₂(33%)/Ar flow for 10 hours at 350°C. The reaction conditions were: 220°C, 24 atm (2.4MPa), H₂/CO = 2/1, 3 NL/hr/g catalyst total gas flow, 1 NL/hr/g catalyst synthesis gas flow. Analysis of the gaseous products was accomplished using gas chromatography.

Results

The conversion of CO and CO₂ during 10 days on-stream are given in figure 1. Compared to the CO conversions of the same and another similar Co-silica catalyst, it appears that the initial CO conversion is about the same in the CSTR and in the fixed bed reactor; however, the activity decline is more rapid in the fixed bed reactor. The run data and conversions for the fixed bed reactor are compiled in table 1.

There was a decline in activity during the period between collecting the first two samples. The exit gas from the CO₂ conversions contained more CO₂ than the calibration gas so that CO₂ conversions were calculated from the mass balance for the other gaseous and liquid products; thus, there is some uncertainty in the absolute CO₂ conversion data but the trend shown

in Table 1 and figure 1 is certainly valid. Thus, with the cobalt catalyst the conversion of CO and CO₂ occur at about the same rate. This is in contrast to the observations with an iron catalyst under low temperature FTS conditions where the rate of conversion of CO₂ is considerably lower than for CO (1-6).

A striking difference for the cobalt catalyst is the formation of methane. Under the same reaction conditions, the amount of methane produced is much higher for the CO₂ reactant (figure 2). Whenever CO₂ was the reactant, methane accounted for greater than 70% (based on carbon) of the products. However, under the same reaction conditions and with the same catalyst, methane accounted for less than 10% of the products with CO as reactant. Similar results are reported by Riedel et al. (6). This requires that methane be formed by two pathways or that a common reaction intermediate and reaction pathway does not occur with CO and CO₂.

During period 9, the feed was changes so that equal amounts of CO and CO₂ were present in the feed and the flows of Ar, H₂ and (CO + CO₂) were the same as when either pure CO or CO₂ was converted. Under competitive conversions, CO was converted much more rapidly than CO₂, clearly showing that CO is adsorbed on the Co catalyst to a much greater extent than the CO₂. Whereas the total carbon oxide conversion is about the same expected from the trend of the previous runs, the conversion of CO accounted for more than 90% of the total conversion of the carbon oxides. A similar result was obtained following the conversion of methanol except that there was not as dramatic a difference as would be expected from the trend of the previous conversions. The CO conversion following the period of methanol feed was lower than expected from the trend of the prior periods. Since the water partial pressure was much higher during the conversion of methanol, it is anticipated that irreversible, or slowly reversible, damage of the catalyst occurred during the exposure to the high water partial pressure conditions.

Following the first conversion of the mixture of CO and CO₂, methanol was substituted for the carbon oxides feed. Because of the limitations of the liquid pump, the feed during this period was only H₂ and methanol. The total flow was 4 NL/hr/g catalyst and the H₂/methanol molar ratio was 2/1. Thus, the H₂/carbon ratio in the feed was the same as when CO and/or CO₂ was the feed but the flow rate of methanol was four times that of the carbon oxide. Under the reaction conditions used the conversion of methanol was about 50% whereas the conversion of CO or CO₂ was slightly less than 25%. Thus, considering the higher flow rate (4 times higher) and higher conversion (2 times higher) of methanol, the total carbon converted with the methanol feed was about 8 times greater than for the carbon oxides. Thus, the relative rate is rapid enough that any methanol intermediate could be converted to methane so that methanol would not be detected in the liquid sample; unfortunately, in this preliminary run the analysis of the gas sample did not provide a measure of the amount of methanol in the gas phase. The only significant products from the conversion of methanol under the FTS conditions were methane and water; thus, any methanol formed during the reaction could have been converted to methane.

Discussion

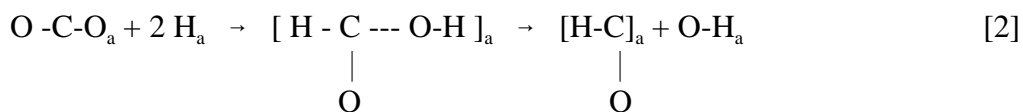
The difference in the product distributions obtained from the hydrogenation of CO and CO₂ preclude a common reaction pathway for FTS unless there is a second reaction pathway for the conversion of CO₂, but not CO, to methane. Furthermore, if there is a second pathway, then the FTS with CO₂ occurs at about only 20% of the rate for CO.

Based on the preliminary data, it is proposed that the conversion of CO and CO₂ occurs by different reaction pathways. It is assumed that the hydrogenation and breaking of the two C-O bonds of the CO₂ provide the source of the different pathways. In this proposal, the breaking of the C-O bond, presumably by the addition of adsorbed H to form C-O-H, competes

with, and probably leads, the addition of adsorbed H to form the C-H bond. Thus, for CO the following reaction pathway could apply:



In the case of CO₂ the reaction is more complex since there are two C-O bonds that must be broken prior to, or simultaneous with, the formation of the C-H bond. If it is assumed that similar rates apply for the formation of the first O-H and C-H bonds as in the case of CO we would have a different situation, idealized in reaction [2]:



If reaction [2] is valid, it is then a matter of the hydrogenation of the adsorbed oxygen species to produce the adsorbed intermediate (methanol) and its subsequent hydrogenation:



Based on the carbon mass balance, about 75% of the hydrogenation of CO₂ would proceed by reaction [3] and the remainder would involve the breaking of the second C-O bond to continue along the normal FTS reaction pathway that is followed by CO hydrogenation. At this time, while the above mechanism accounts for the products that are produced from the hydrogenation of CO₂, it is very speculative. ¹⁴C-tracer studies are planned that should provide some evidence to establish whether the speculation has merit.

The results to date for the hydrogenation of CO₂ indicate that it will not be commercially attractive using typical FTS catalysts based on iron or cobalt.

References

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Table 1

Run Conditions and Results from the Conversion of CO and CO₂ with a Cobalt-silica Catalyst

Sample No.	Time on Stream(hrs)	Feed Gas	Conversion(%)
1	17.3	CO	52.2
2	39.47	CO	45.8
3	44.47	CO ₂	31.2
4	61.97	CO	24.4
5	70.47	CO ₂	23.1
6	90.97	CO ₂	20.5
7	109.97	CO	18.6
8	117.22	CO ₂	24.5
9	134.47	CO+CO ₂	CO, 53.5% CO ₂ , 3.98%
10		methanol	
11	206.22	CO+CO ₂ (different flow rate)	CO: 9.86% CO ₂ : 6.1%
12	226.89	CO ₂	22.8

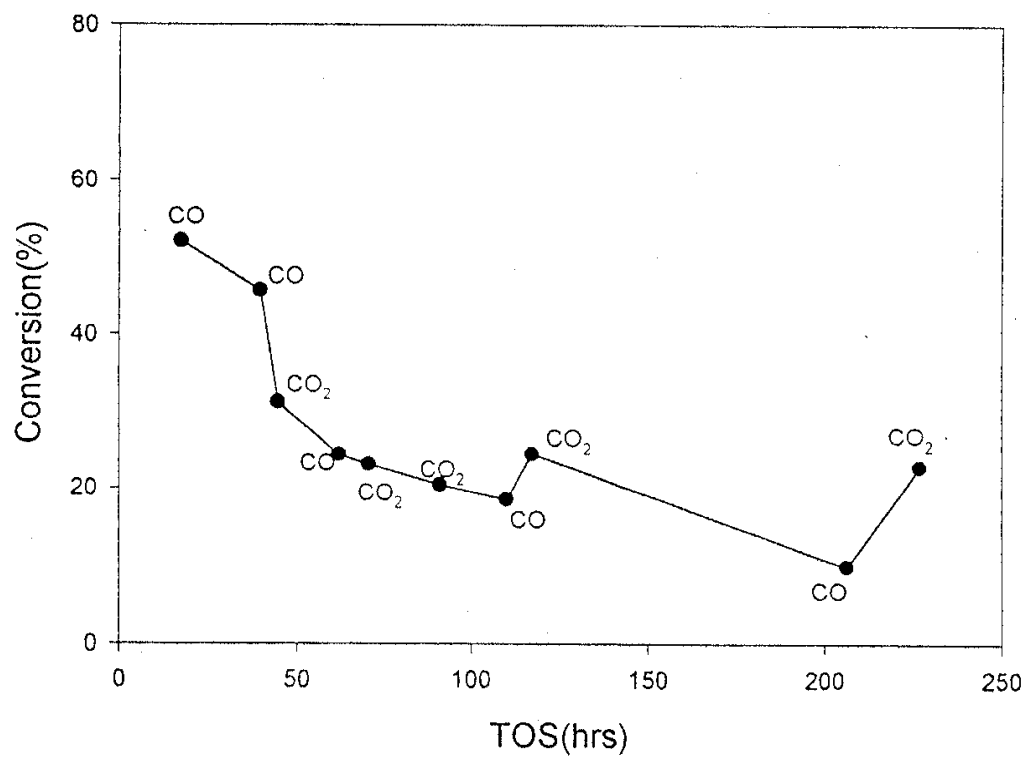


Fig.1 CO and CO₂ conversion as a function of time on stream

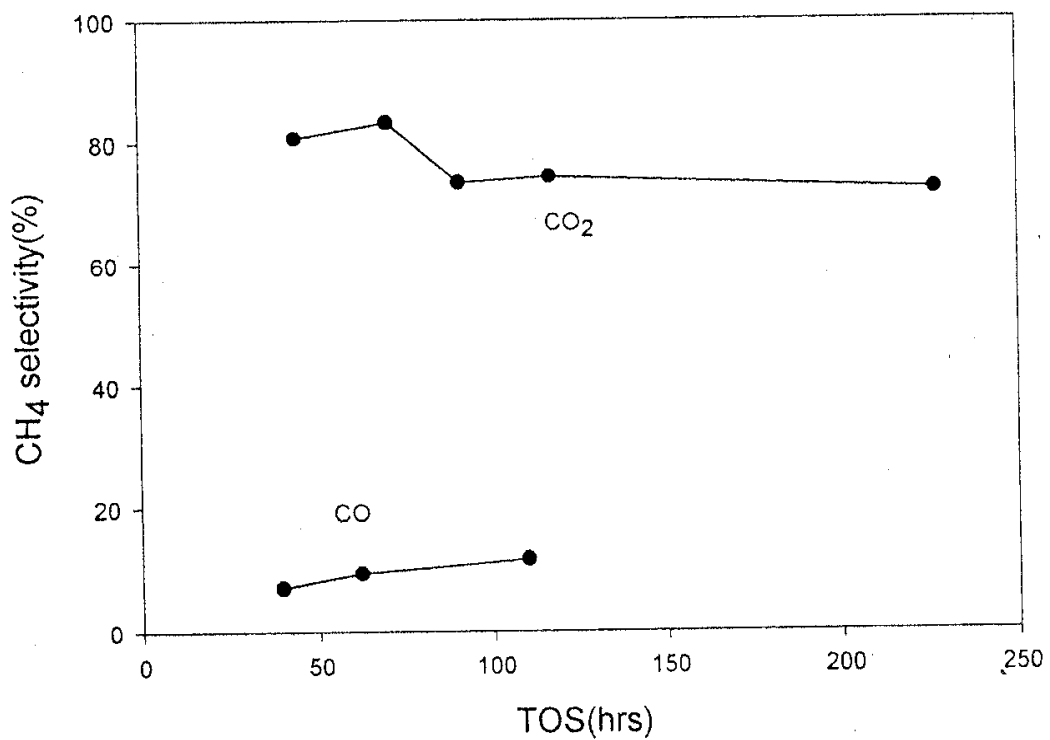


Fig. 2 Methane selectivity as a function of time on stream

C. CO and CO₂ Hydrogenation over Co-Pt/Al₂O₃ Catalyst

Introduction

The feed syngas from natural gas contains a small amount of CO₂, the effect of CO₂ therefore should be studied to determine the necessity of separation of CO₂ from syngas. Study of CO₂ hydrogenation will also help us understand the mechanism for methane formation. CO₂ methanation is important in production of substitute natural gas, since it contributes additional methane needed to meet heating value specifications. Two categories of mechanisms for CO₂ hydrogenation has been proposed based on the early work done on nickel catalysts, (1) conversion of CO₂ to CO via the reverse water gas shift reaction followed by CO methanation, and (2) direct hydrogenation of CO₂ to methane by a mechanism distinct from CO methanation.

Previous works on CO and CO₂ hydrogenation of our group leads to the conclusion that CO hydrogenation rate is much higher than CO₂ over cobalt catalyst and CO₂ methanation goes through methanol as an intermediate.

The purpose of this investigation is to determine the deactivation rate for CO₂ hydrogenation at different H₂:CO ratio and different conversion level, as well as the deactivation rate of CO hydrogenation. We would probably have a better understanding of the mechanism of deactivation.

Experimental

Preparation of Co-Pt/Al₂O₃

Condea vista B alumina with a surface area of 300m²/g, pore volume of 1.15m³/g was used as support materials and the cobalt loading was 15%. A multi-step incipient wetness impregnation method was used to add cobalt nitrate solution to alumina with a drying procedure after each impregnation at 80⁰C in a rotary evaporator. Following cobalt addition, tetramineplatinum nitrate solution was added by an incipient wetness impregnation method and

the platinum loading was 0.5%. The catalyst was then dried in a rotary evaporator at 80°C again and calcined at 400°C for 4hrs.

Fixed-bed Fischer-Tropsch Synthesis Study

3g of Co-Pt/Al₂O₃ catalyst was diluted by 15g of glass bead and then loaded in a two inch diameter reactor, a three zone furnace was used to control the temperature of the reactor. Four Brooks mass flow controllers were used to control the flow rate of CO, CO₂, H₂ and He. Fischer-Tropsch synthesis was conducted at 210°C, 350psig with H₂:CO=2:1 and GHSV=5.0SL/hr/gcatalyst(H₂:CO:He=2:1:2). CO₂ hydrogenation was tested at same temperature and pressure but with H₂:CO ratio of both 2:1(H₂:CO:He=2:1:2) and 4:1(H₂:CO₂:He=4:1:4). The space velocity was changed from 9.0SL/hr/gcatalyst to 5.0 SL/hr/gcatalyst.

Results and Discussion

Since we use H₂:CO ratio of 2:1 as the feed gas, the highest CO₂ conversion is 50%. At time on stream 48hr, CO₂ conversion observed was 45% which is close to equilibrium. The fact that the conversion decreased at 0.81% CO₂ conversion per day indicated that the catalyst is reasonably stable for CO₂ hydrogenation. In order to investigate the stability of catalyst far from equilibrium, we increased the flow rate from 5.0SL/hr/gcatalyst to 9.0SL/hr/gcatalyst. The deactivation rate became even lower(from 0.81% to 0.69% CO₂ conversion per day) and the activity range maintained at about 20% CO₂ conversion range.

One of the assumptions for the deactivation mechanism of cobalt Fischer-Tropsch synthesis catalyst is the oxidation of surface cobalt to oxide or cobalt aluminate by water. Our assumption of the oxidation mechanism is that when H₂O/H₂ partial pressure ratio goes up to certain point, the oxidation of the cobalt cluster starts to occur. For CO₂ hydrogenation when the conversion level is at 40%, the H₂O/H₂ partial pressure ratio is about 2.0 and is much higher than CO hydrogenation (0.3 at 40% CO conversion). But for CO₂ hydrogenation, the deactivation is

not so obvious (figure 1 is the CO_2 conversion as a function of time on stream). One explanation is that the oxidation only occurs to the small clusters and the methanation of CO_2 is catalyzed by the larger cobalt clusters. The other explanation is that the surface oxidation did not occur as fast as CO hydrogenation. That makes the assumption of $\text{H}_2\text{O}/\text{H}_2$ partial pressure ratio as the decisive factor for the oxidation invalid. It also brings up another explanation of the deactivation of CO hydrogenation, which is $\text{H}_2\text{O}/\text{CO}$ ratio is a more important factor. One possibility is that the adsorption of H_2O and CO are competitive and since more H_2O has been formed, the less CO can be adsorbed. But the results of CO_2 hydrogenation eliminate that possibility; therefore, one can conclude that H_2O and CO has formed some kind of intermediate which caused the oxidation or crystal growth of cobalt clusters.

Since the methanation of CO_2 requires $\text{H}_2:\text{CO}$ ratio of 4:1, we adjusted the feed gas to this ratio to further study the stability of the catalyst and the results are shown in figure 2. When the conversion level is 42%, the catalyst did not deactivate after 24hrs, then the flow rate was decreased to achieve a conversion of about 55%; the catalyst started to deactivate slowly but leveled off at about 40% CO_2 conversion. It can be concluded that during CO_2 hydrogenation, deactivation is slower than for CO hydrogenation even at high conversion levels.

After 504 hours of using CO_2 as a feed gas, CO hydrogenation was studied with a $\text{H}_2:\text{CO}$ ratio of 2:1 and space velocity of 5SL/hr/gcatalyst. Figure 3 shows the results of CO conversion as a function of time on stream, and figure 4 is CO and CO_2 conversion as a function of time on stream when CO was used as the feed gas first. It can be concluded that CO_2 hydrogenation did cause deactivation of the catalyst for subsequent CO hydrogenation since, after 504 hours of time on stream, CO conversion decreased from 52.5% to 28.7%. However, it can be seen from figure 3 that the deactivation rate of CO hydrogenation is much faster than CO_2 hydrogenation at 30% CO conversion. If the feed gas is CO and the conversion is 60%, the

deactivation rate could have been much higher and after 504 hours of time on stream, CO conversion rate would have been much lower than 28.7%. From figure 3, it seems that the CO conversion stayed at about 20% and it agrees with our CSTR data that the deactivation rate is a function of CO conversion level; the lower the CO conversion, the lower the deactivation rate.

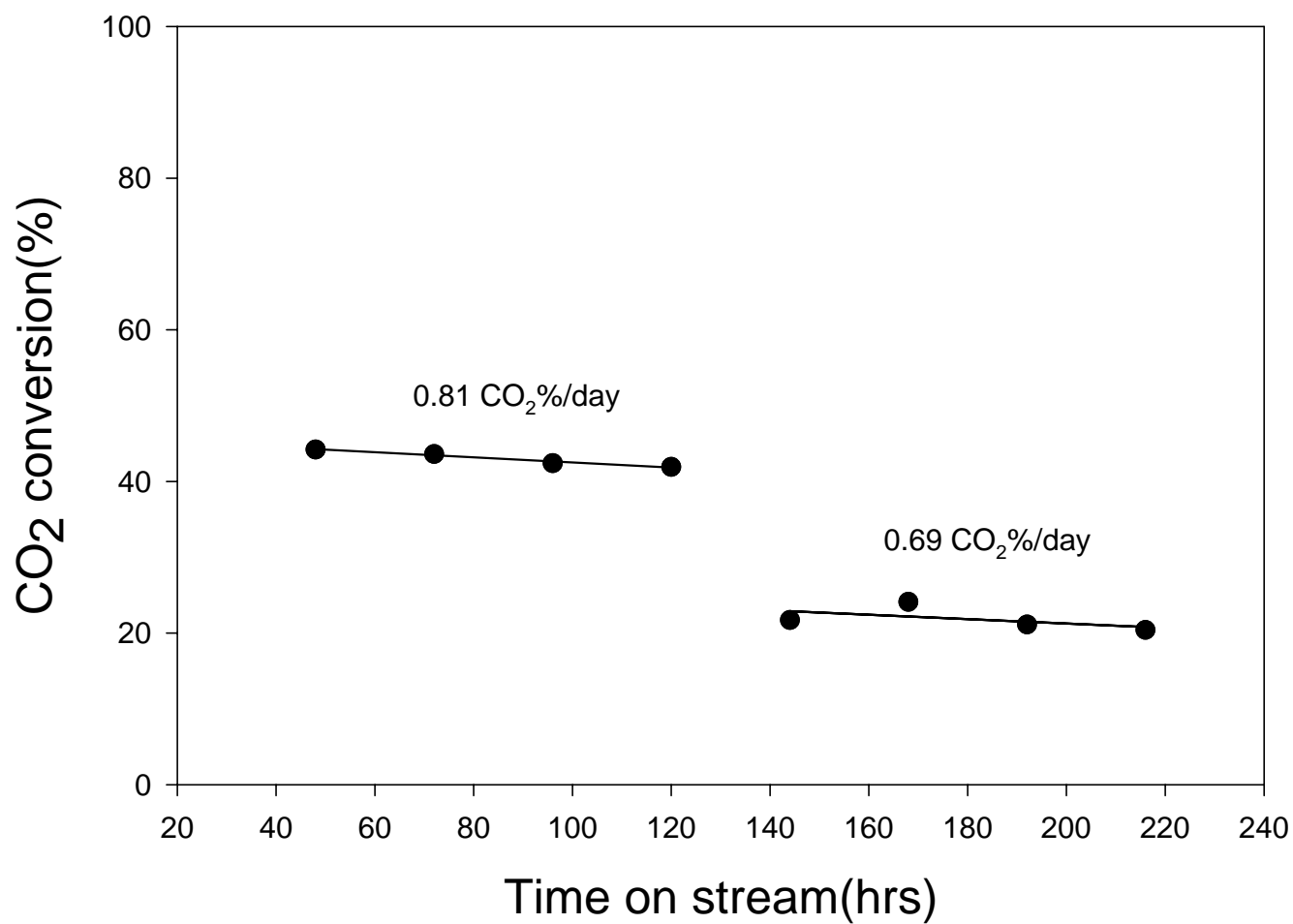


Figure 1. CO₂ hydrogenation over Co-Pt/Al₂O₃, 210°C, 350psig, H₂:CO=2:1, GHSV=5.0SL/hr/gcatalyst.

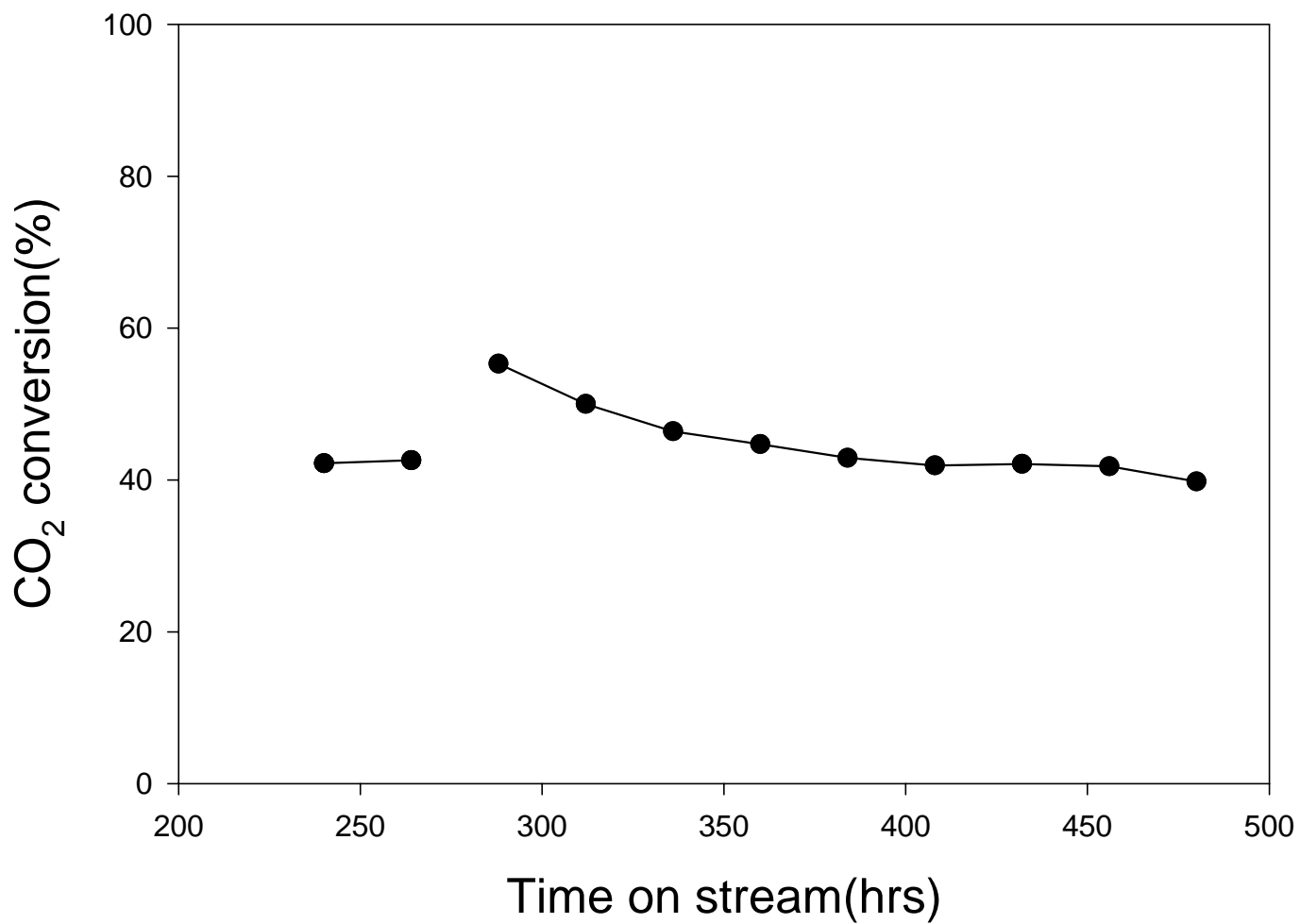


Figure 2. CO₂ hydrogenation over Co-Pt/Al₂O₃ at 210°C, 350psig, H₂:CO=4:1, GHSV=9.0 and 5.0SL/hr/gcatalyst.

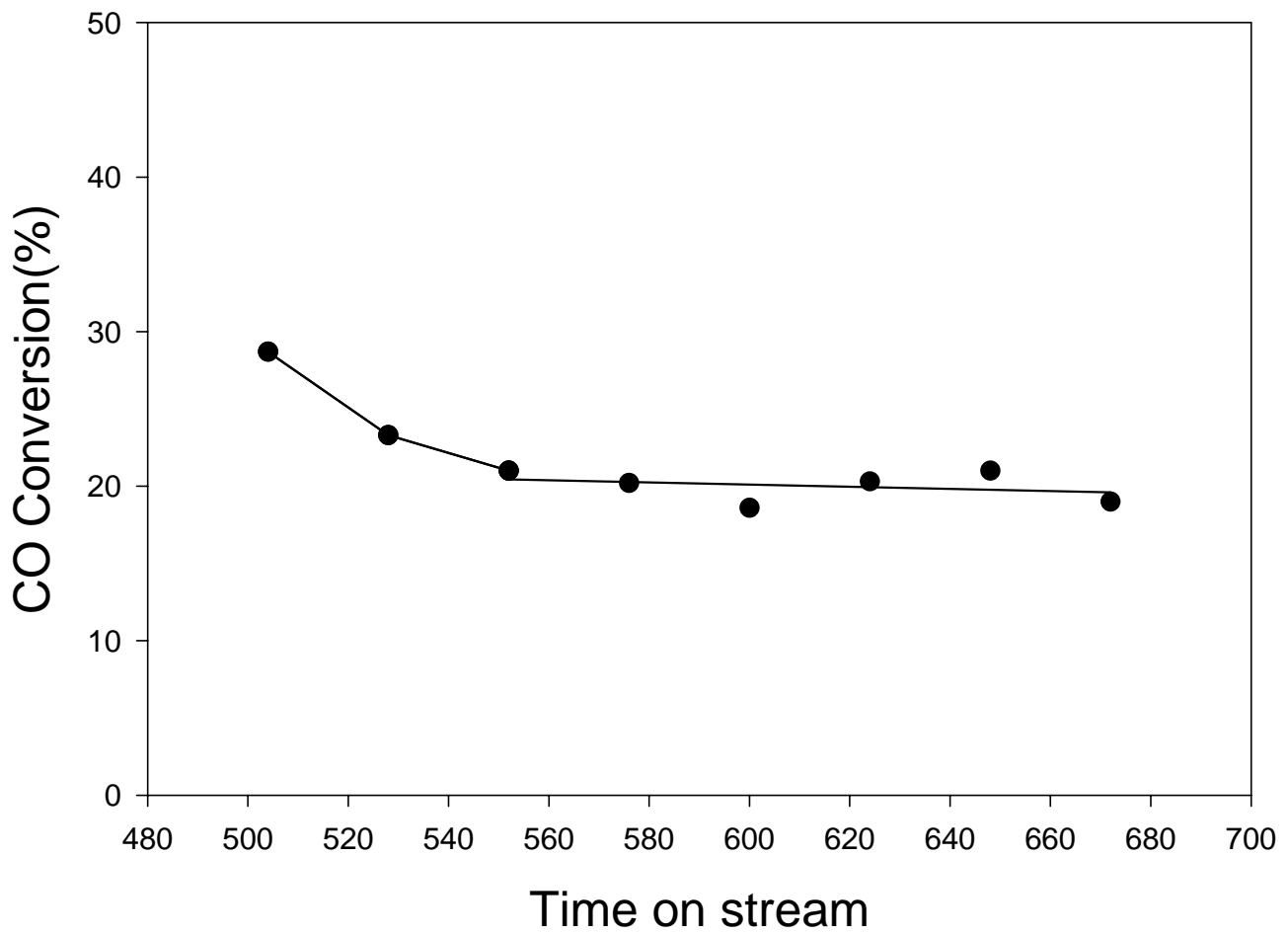


Figure 3. CO hydrogenation over Co-Pt/Al₂O₃ at 210°C, 350psig, H₂:CO=2:1, GHSV=5.0SL/hr/gcatalyst.

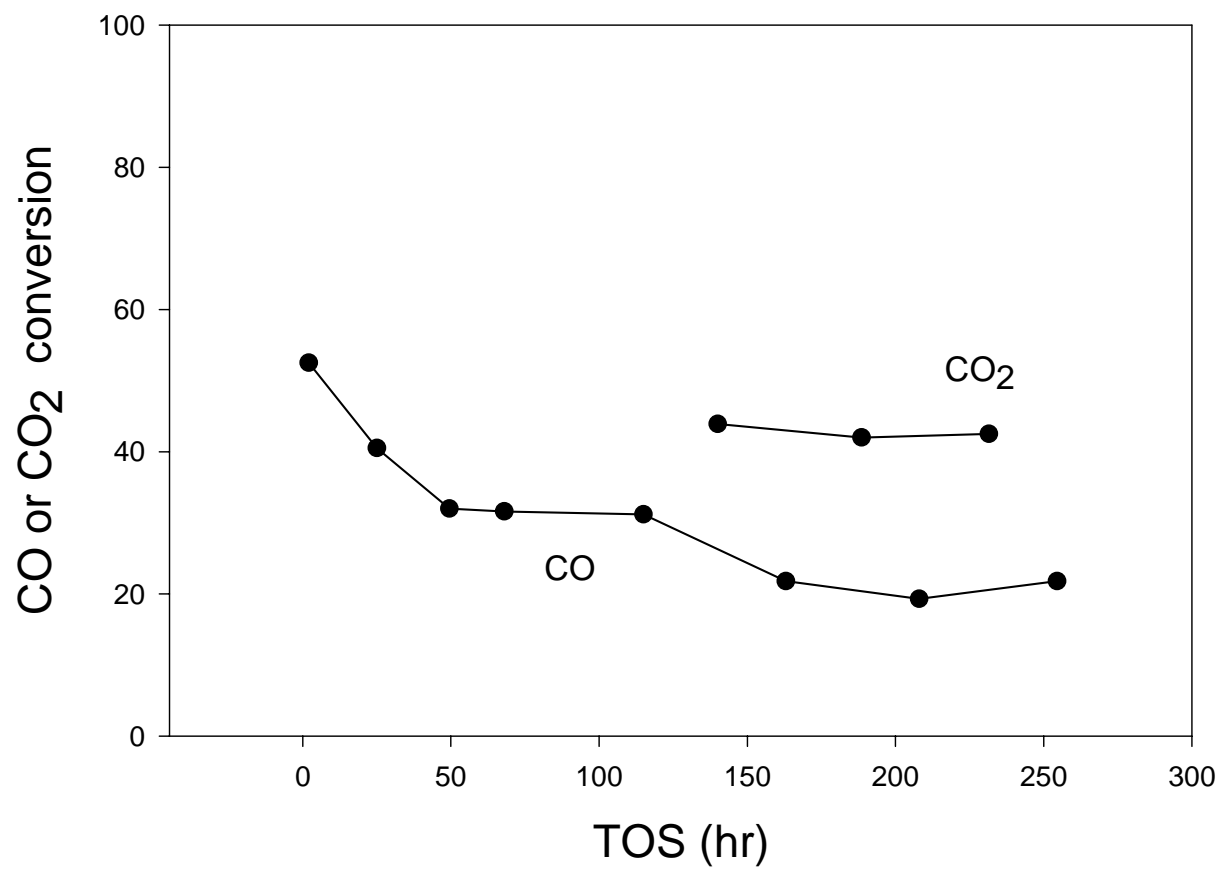


Figure 4. CO or CO₂ conversion as a function of time on stream

D. The CSTR studies of Co(10)/B(x)/TiO₂ Fischer-Tropsch catalysts

1. Reaction system

A 1-liter autoclave, 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/TiO₂ and 10 wt% Co/ 0.05% B/TiO₂, 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⁻¹gcat.⁻¹ (25°C, 0.1 mPa). The reactor temperature was increased to 280°C at a rate 120°C h⁻¹ 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⁻¹ gcat.⁻¹ at a constant H₂/CO ratio of 2. Afterwards, the H₂/CO ratio synthesis gas was varied from 2 to 5 at a constant space velocity of 2 NL h⁻¹gcat.⁻¹. 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 H₂/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.

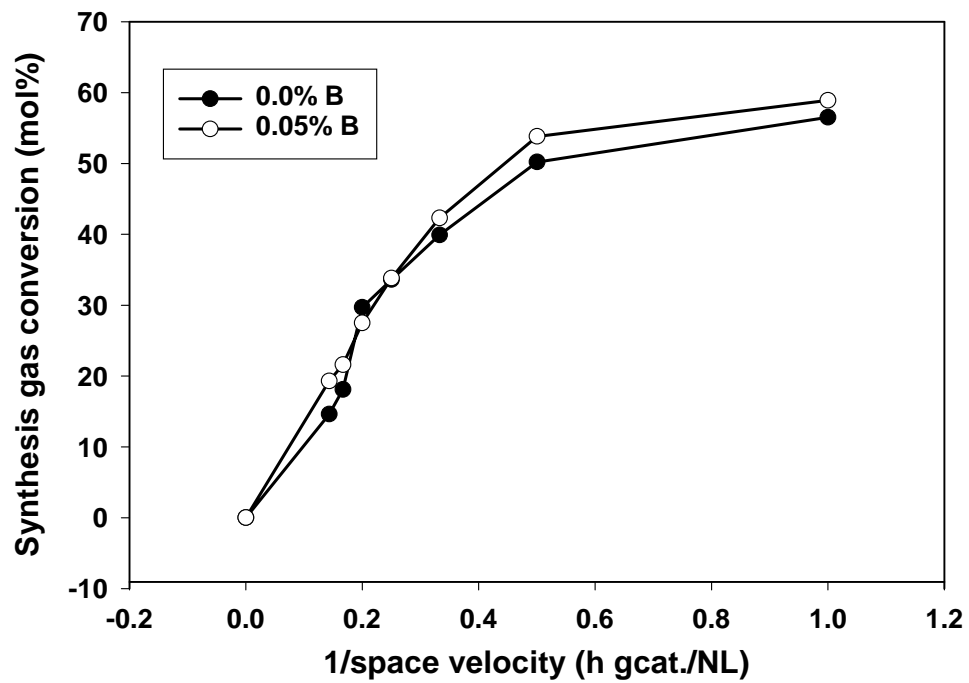


Figure 1. Synthesis gas conversion as a function of reciprocal flow rate

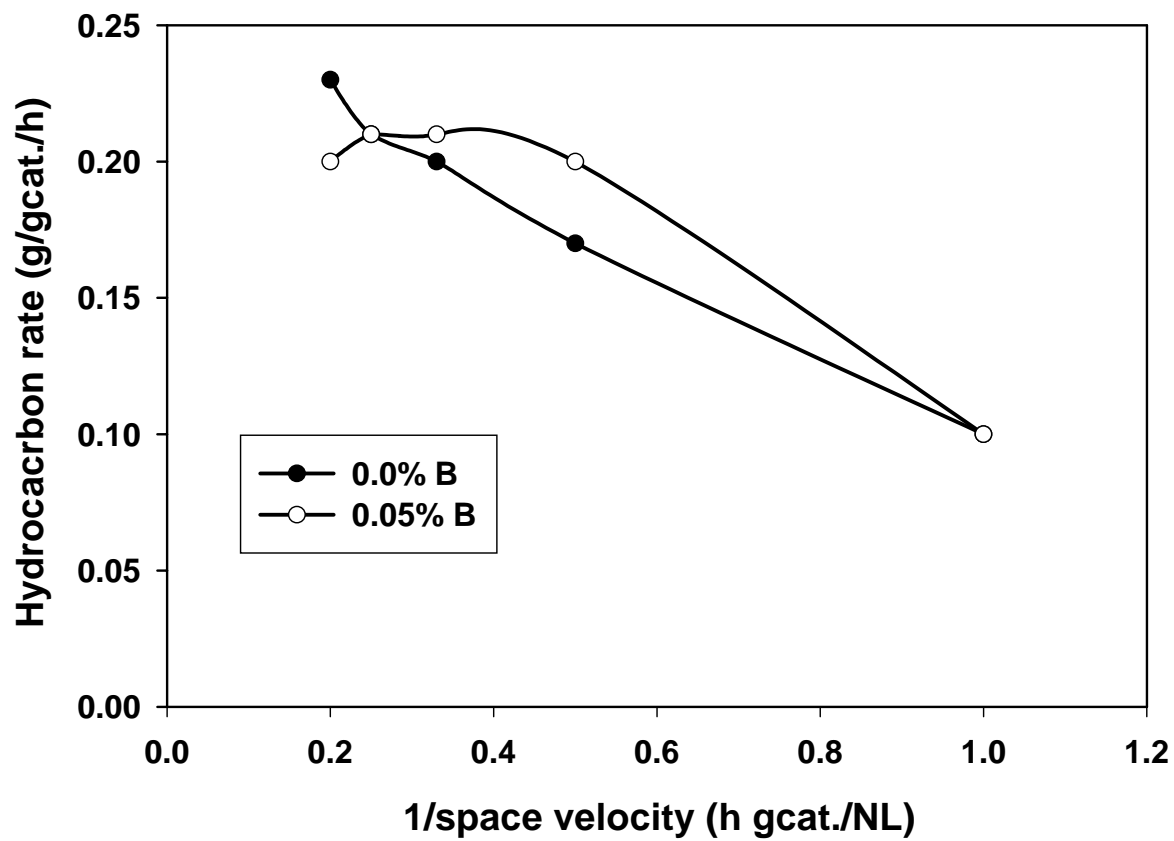


Figure 2. Hydrocarbon production rate as a function of reciprocal flow rate

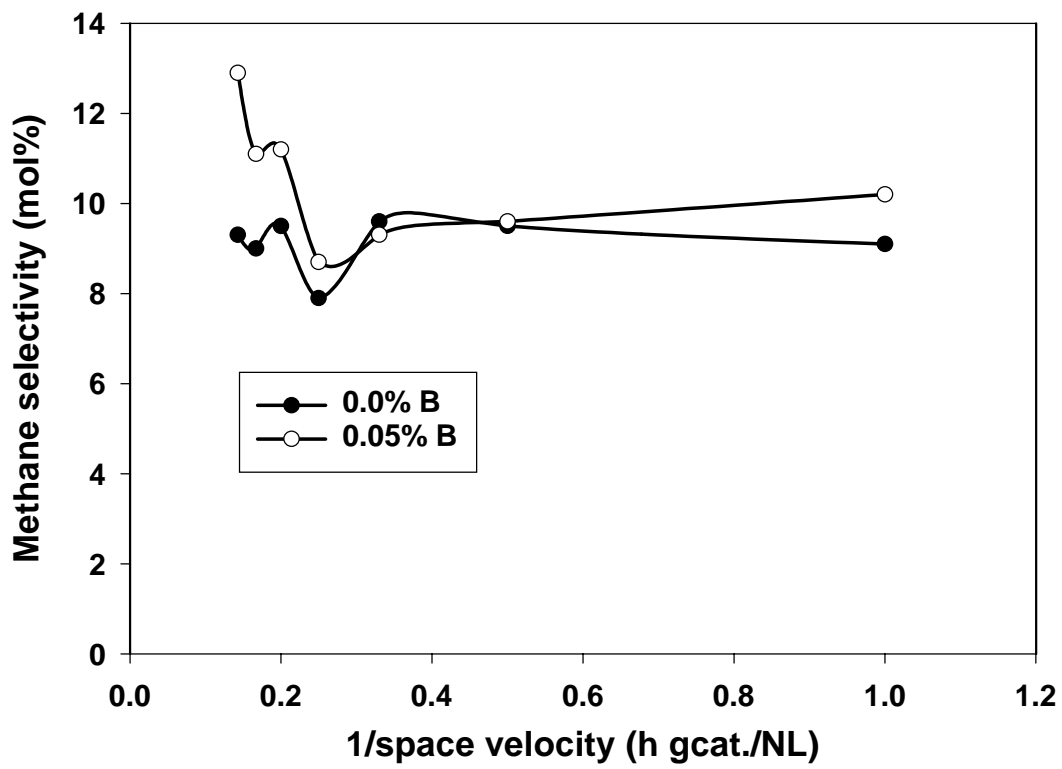
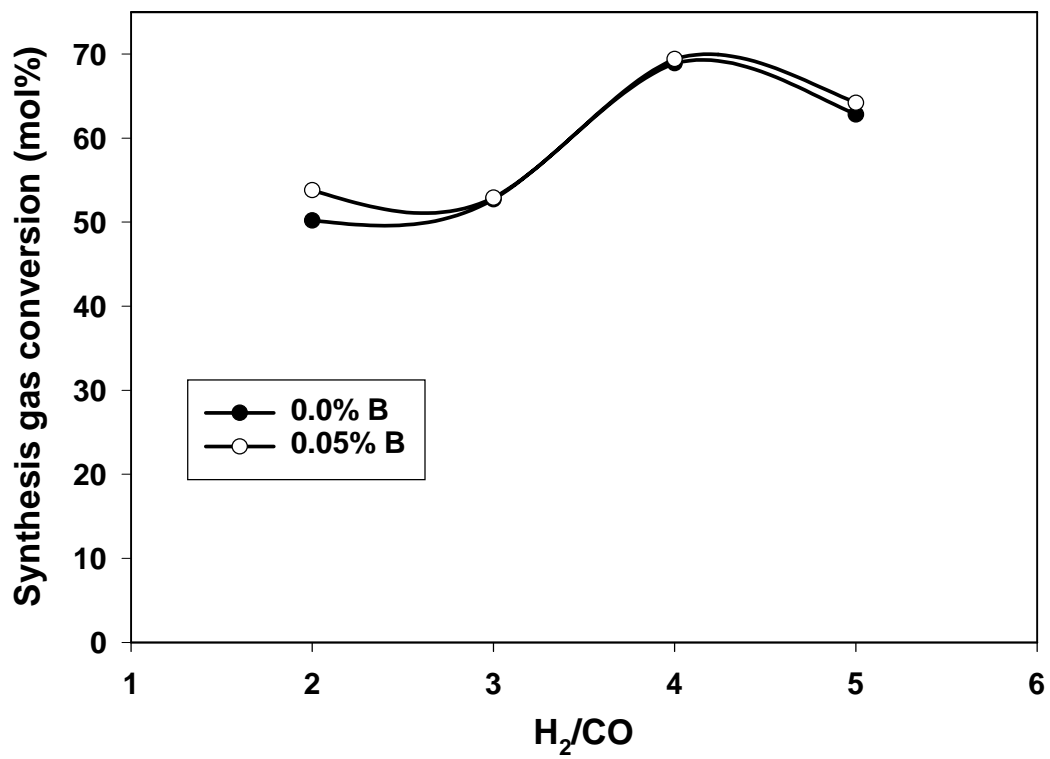
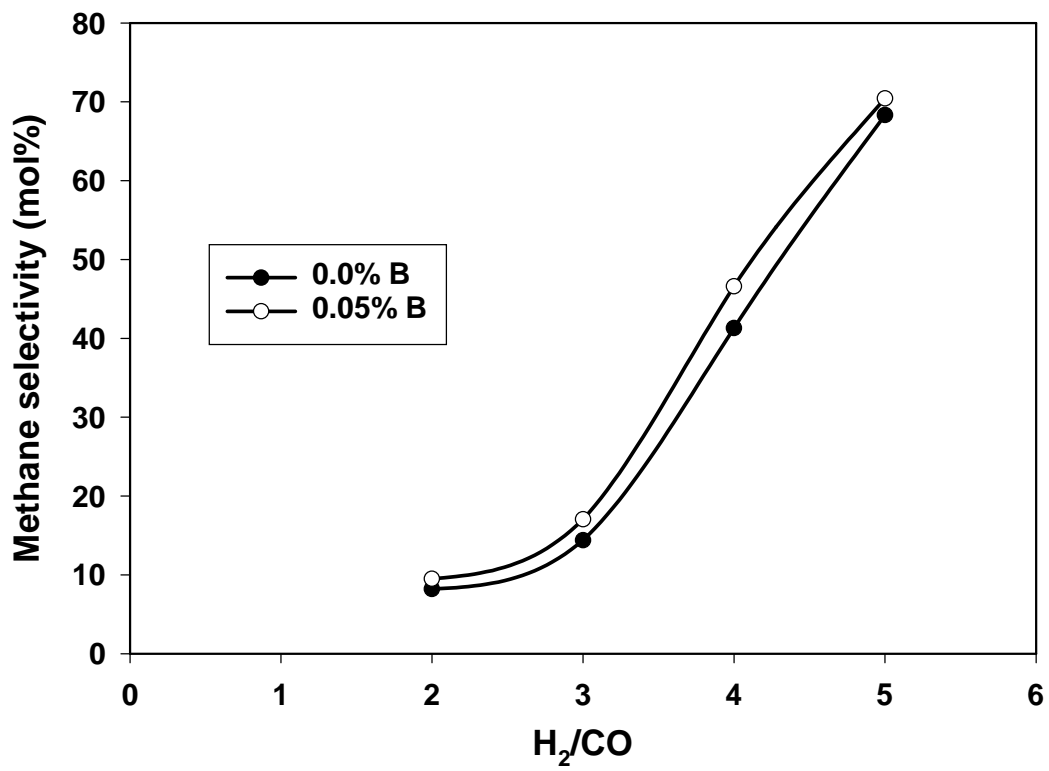


Figure 3. Methane selectivity vs reciprocal flow rate



**Figure 4. Synthesis gas conversion vs ratio of H₂ to CO
(at SV=2 NL/gcat./h)**



**Figure 5. Methane selectivity vs ratio of H₂ to CO
(at SV=2 NL/gcat./h)**

E. 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 he

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/SiO₂ 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/SiO₂ catalyst was prepared by incipient wetness impregnation method using Davisil 644 Silica gel as support (surface area 300m²/g, pore volume: 1.15cm³/g, particle size 100-200mesh) 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 repressurize 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 cause 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 30min and held at 100°C for 30min, and after that the temperature was increased to 350°C with at a rate of 1°C/min, then held at 350°C for 15hrs.

Reaction conditions:

Conditions	P _{overall} (MPa)	P _{syngas} (Mpa) H ₂ :CO =2.0	P _{solvent} +P _{He} (MPa)	T(°C)	Total Flow Rate (ml/min)	Syngas Flow Rate (ml/min)	He Flow Rate (ml/min)	Solvent Fow 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°C; therefore, the critical temperature of the solvent chosen should be below 220°C. Since the critical temperature for n-pentane is 197°C and for n-hexane is 232°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 220⁰C.

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 220⁰C (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 160⁰C and 0⁰C 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 α value of the reaction has not been defined. Nevertheless, the selectivities of methane and CO₂ 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 CO₂, 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/SiO₂ 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 α value of different conditions will be defined in future work.

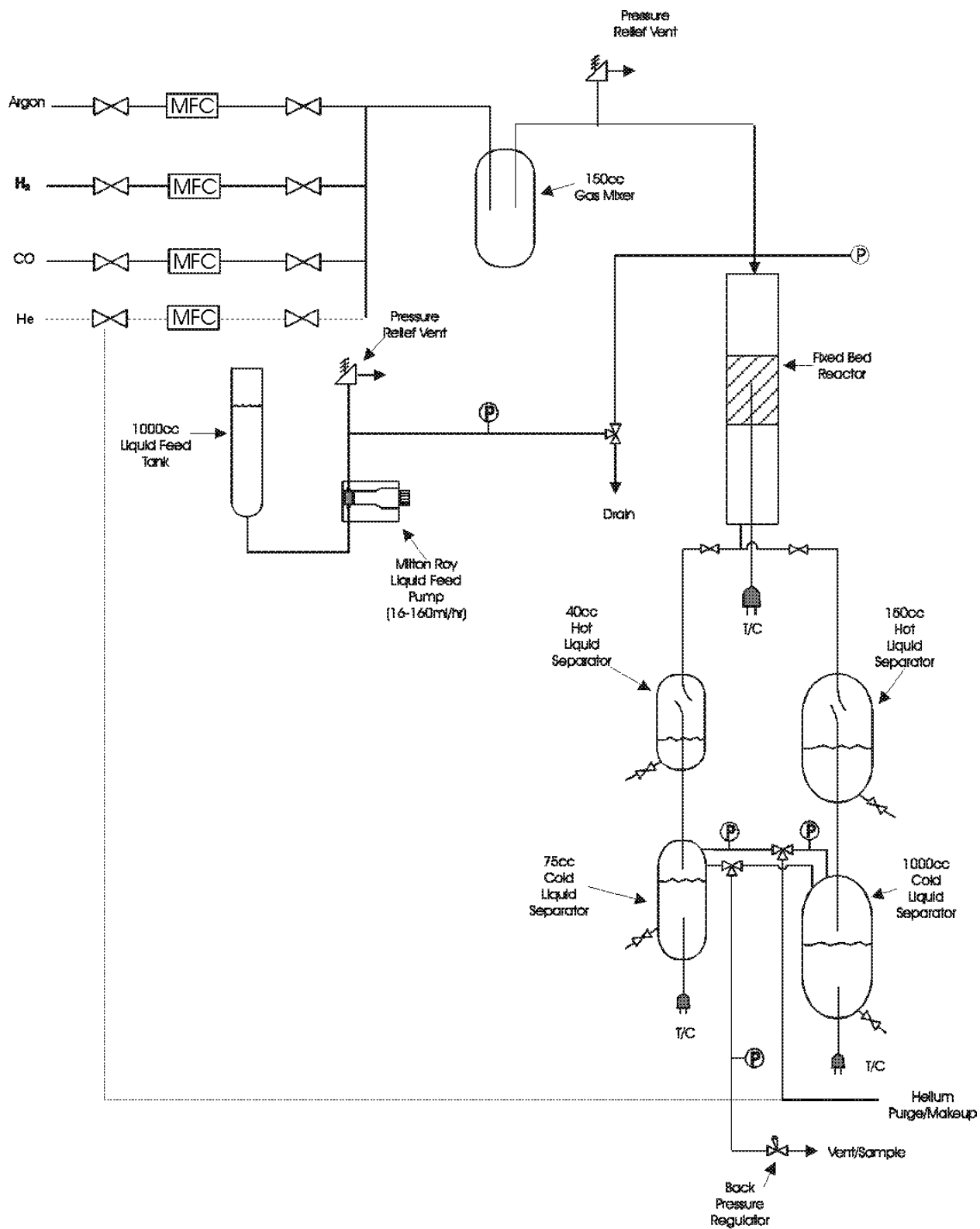


Figure 1. Supercritical FT Reactor-Flow Diagram

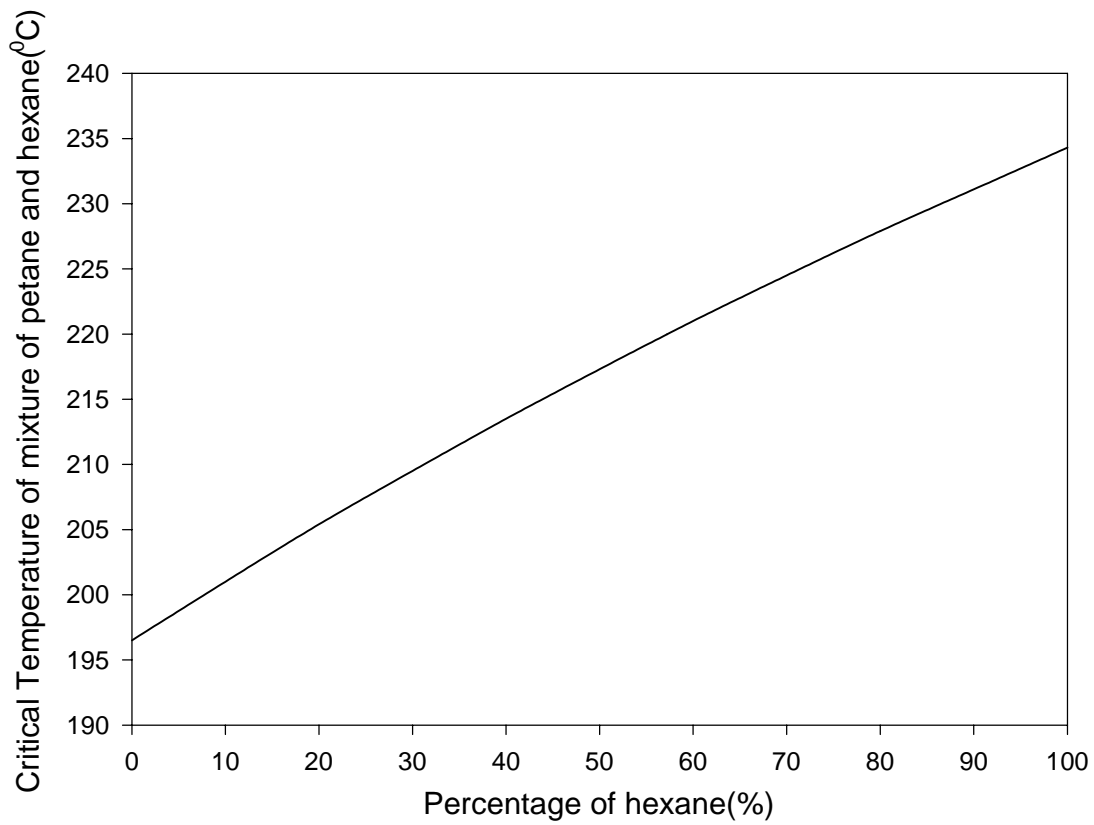


Figure 2. Critical temperature of pentane and hexane mixture with hexane percentage.

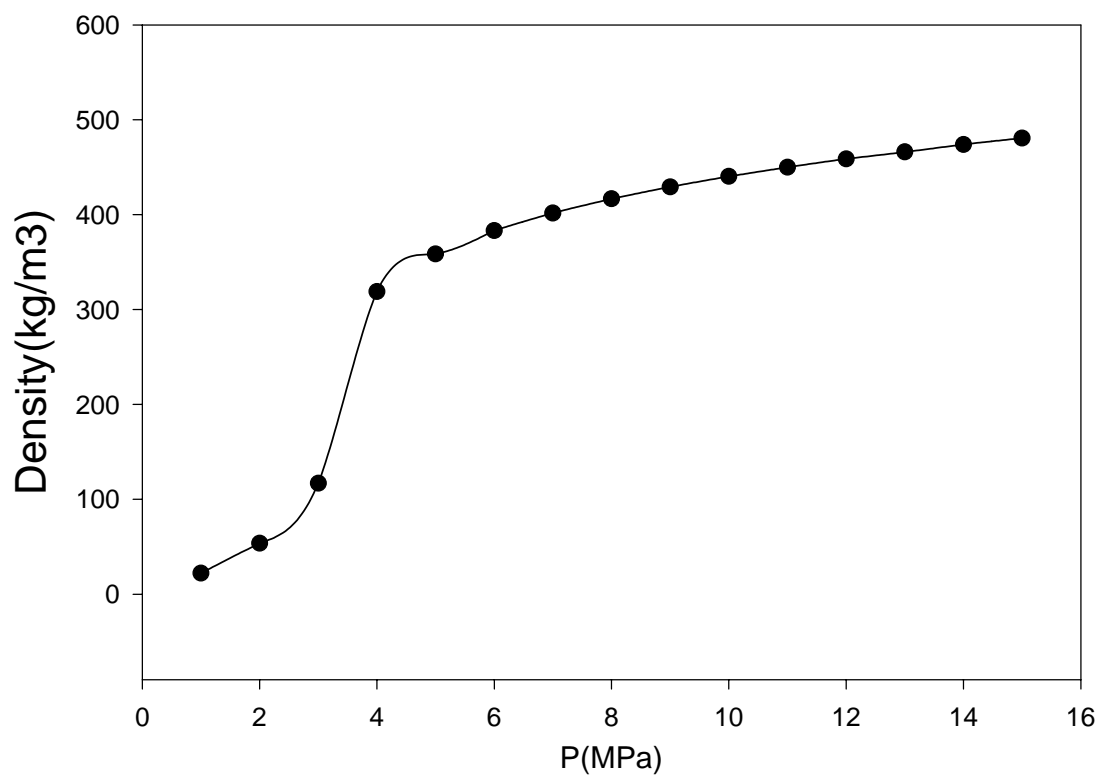


Figure 3. Density vs. pressure mixture of 55%(V) pentane and 45%(V) hexane.

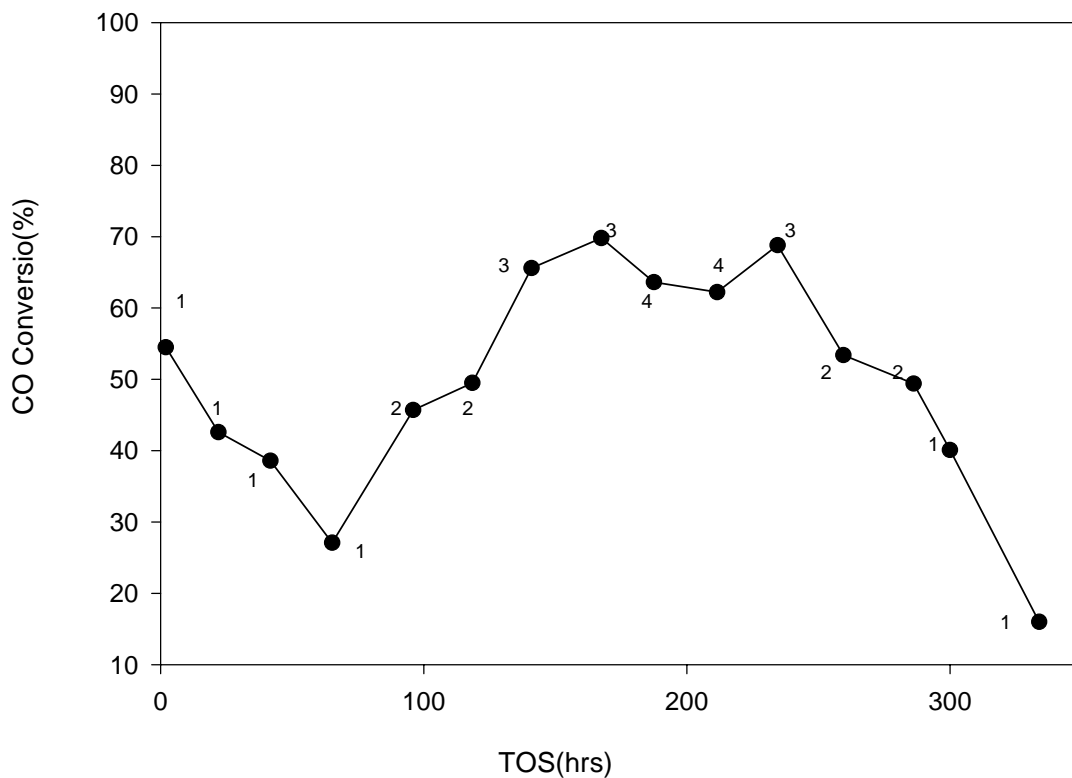


Figure 4. Run YQZ 304. CO conversion vs. TOS ($T = 220^{\circ}\text{C}$, $P_{\text{total}} = 8.0 \text{ mpa}$, $P_{\text{syngas}} = 2.0 \text{ mpa}$, $\text{H}_2:\text{CO} = 2:1$; 1 = $P_{\text{He}} = 6.0$, $P_{\text{C5+C6}} = 0$; 2 = $P_{\text{He}} = 4.0$, $P_{\text{C5+C6}} = 2.0$; 3 = $P_{\text{He}}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

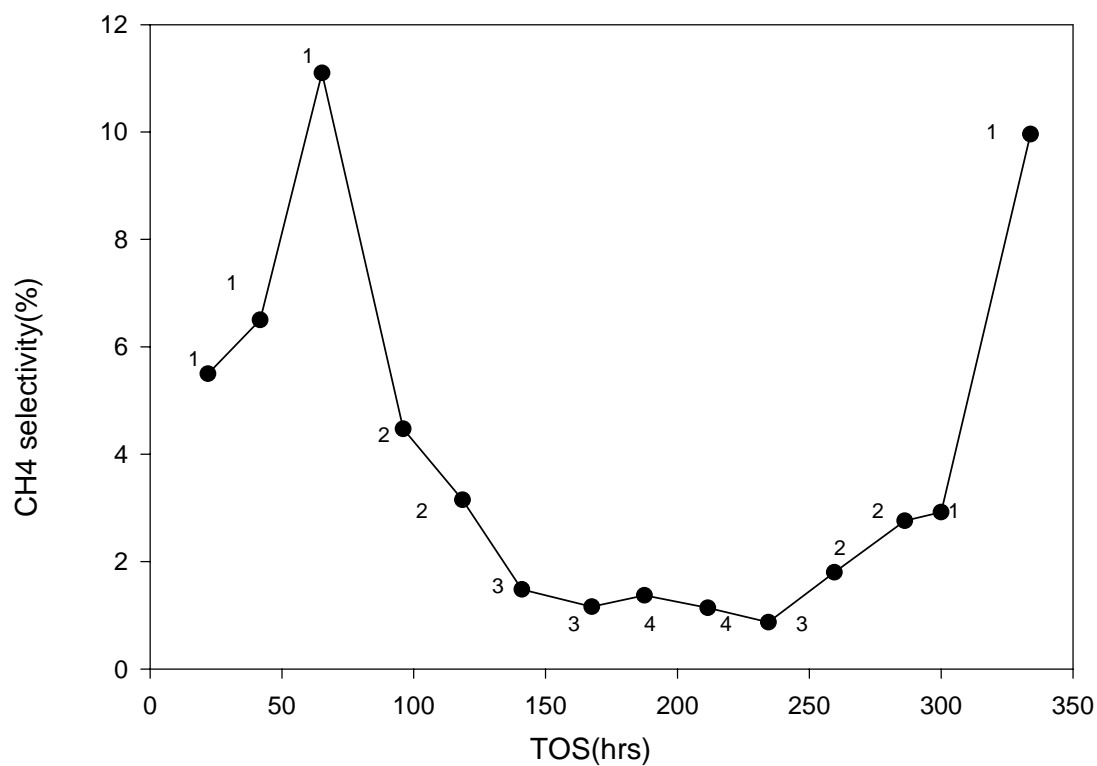


Figure 5. Run YQZ 304. CH₄ selectivity vs. TOS (T = 220°C, P_{total} = 8.0 mpa, P_{syngas} = 2.0 mpa, H₂:CO = 2:1; 1 = P_{He} = 6.0, P_{C5+C6} = 0; 2 = P_{He} = 4.0, P_{C5+C6} = 2.0; 3 = P_{He} = 2.5, P_{C5+C6} = 3.5; 4 = P_{He} = 0, P_{C5+C6} = 6.0).

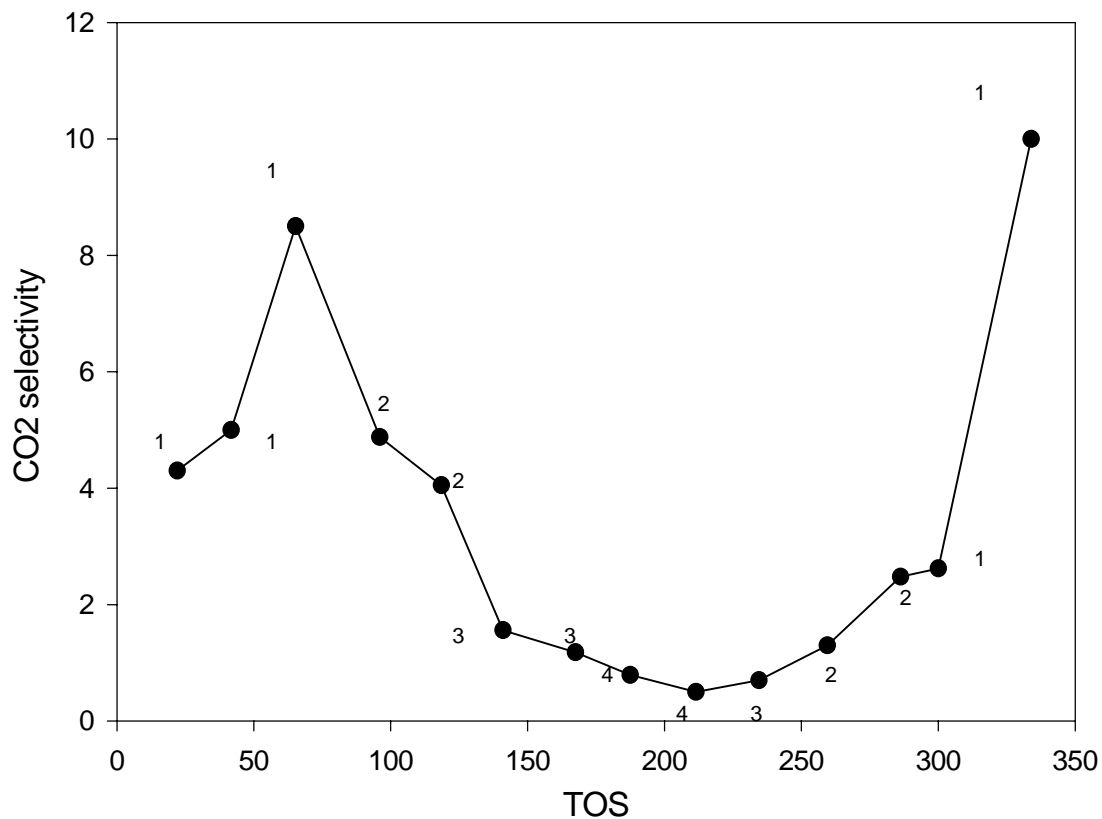


Figure 6. Run YQZ 304. CO₂ selectivity vs. TOS (T = 220^oC, P_{total} = 8.0 mpa, P_{syngas} = 2.0 mpa, H₂:CO = 2:1; 1 = P_{He} = 6.0, P_{C5+C6} = 0; 2 = P_{He} = 4.0, P_{C5+C6} = 2.0; 3 = P_{He} = 2.5, P_{C5+C6} = 3.5; 4 = P_{He} = 0, P_{C5+C6} = 6.0).