

Executive Summary

CAER

Factorial design is an effective approach for studying process parameters. By designing the experiment, the number of trials was minimized and time and expenses were significantly reduced. Although two-level factorial design failed to detect the nonlinearity of the process between the high and low level of factors concerned, it is still the more effective to conduct several two-level experiments than to perform a series of three- or four-level experiments. In addition, two-level factorial design reveals the interactions between factors.

Results from this study shows that temperature had the most important influence on CO and H₂ conversions, CO₂ and CH₄ selectivity and hydrocarbon production rate for the FTS process. Pressure and space velocity played a less significant role in affecting CO and H₂ conversions. Interaction effects of temperature and pressure from beryllium promoted catalyst was significant. A temperature increase from 230 to 270°C significantly raised the CO conversion from ~19 to 35% when potassium promoted catalysts were utilized. Hydrogen conversion was also significantly increased for temperature increase. An increase in temperature from 230 to 270°C resulted in an H₂ conversion increase of 25-27%. Temperature effect on H₂ conversion using Be promoted catalyst was not as important as that using potassium promoted catalysts. Pressure and space velocity effects were found to be much less important than temperature. Only a 2.4 to 6.6% change in CO conversion was found as pressure increased from 1.2 to 2.9 MPa when potassium promoted catalysts were used. Space velocity had a slightly greater effect on CO conversion than pressure and a 13 to 20% increase in CO conversion was found when space velocity was changed from 5 to 10 sl/h/g-Fe.

It is also found that when potassium promoted catalysts were utilized, CH₄ selectivity was not significantly affected by any of these three factors. Temperature had the more important effect on CH₄ selectivity than that of pressure and space velocity. Carbon dioxide selectivity, however, changed more appreciably with the change in reaction temperature. A 16.2 to 19.3% increase in CO₂ was found when temperature was increased from 230 to 270°C when potassium promoted catalysts were used. Pressure and space velocity did not yield an important influence on CO₂ selectivity.

XANES analysis of spent unpromoted and Ru or Pt promoted 15% loaded Co/Al₂O₃ catalysts gave evidence of oxidation of a fraction of the catalyst from water produced during the reaction. From analysis of the pre-edge feature and the XANES derivative spectra, the oxidized clusters showed evidence of a tetrahedral environment, indicating that either Co₃O₄ or Co aluminate was formed. The two are not easily distinguished by either XRD or XANES but comparison of XANES spectra of spent and calcined catalysts and linear combination fitting against reference spectra suggested Co aluminate formation. Because bulk oxidation of Co by water is not permitted by thermodynamics under FTS conditions, the conclusion was that only the very small clusters interacting with the support and deviating from bulk-like behavior oxidized in the presence of water produced during the reaction. TPR and hydrogen chemisorption results indicated that promoting the catalyst with Ru or Pt allowed for the reduction to metal of a fraction of smaller CoO clusters which were not reduced for the unpromoted catalyst. The resulting smaller metal clusters deviated even more from the bulk; therefore, the promoted catalyst was more susceptible to reoxidation, as indicated by reaction testing. While the catalyst displayed higher initial activity due to the presence of a greater

number of active sites from enhanced reducibility, the deactivation rates for these catalysts were faster than the unpromoted catalyst.

Measured high alpha catalyst deactivation rates in the SBCR system were comparable to that of CSTR experiments under similar conditions. As observed in previous pilot plant tests, the SBCR exhibited properties of a plug-flow reactor as evidenced by its higher gas conversion and the more olefinic properties of the F-T products as compared to that of the CSTR. Overall alpha distributions between the two reactor systems were quite similar.

Attrition tests in the SBCR system indicated that the most of the catalyst breakdown occurred between the time period of loading and activation; however, further research will be required to investigate the possibility of particle size classification/segregation at the sampling points. After activation, the catalyst particle mean diameter decreased in an exponential decay fashion.

A decreased gas hold-up within the SBCR was found to be the main cause of losing slurry level after changing the H_2/CO ratio from 0.7 to 2.0. Lighter gas bubbles and changes in the reactor wax over time could influence average bubble rise velocity.

UC/B

In this reporting period, the research effort emphasized the preparation of a manuscript entitled “Catalyst Design and Control of Site Density for Fe-Based Fischer-Tropsch Synthesis”, which described a systematic catalyst design route for FTS reactions through the study of the promoter effect of Cu and Ru on the site density and catalytic performance of Fe-Zn catalysts. The replacement of Cu by Ru in the Fe-Zn-K matrix increased the reduction/carburization of Fe oxides, leading to a larger number of nucleation sites for the formation of smaller Fe carbide species. These active species provide higher density of sites for CO adsorption/dissociation and

hence higher FTS rates. Based on these promoter effects, a high surface area, high activity Fe-Zn-K-Cu catalyst was synthesized by an appropriate choice of solvent used in the drying step of the precursor preparation. The observed increase in FTS activity appears to correlate well with higher density of active sites. The rates on this high surface area Fe-Zn-Cu-K catalyst are comparable with the best-reported values in the literature for FTS reactions using a natural gas-derived synthesis gas at higher temperatures. It also exhibits good performance at low temperatures typically employed for Co-FTS catalysts. Hydrocarbon productivities resemble with those on a Co/SiO₂ catalyst at 473 K and 2140 kPa.

Experiments with the high surface area Fe-Zn-Cu-K (Zn/Fe=0.1, Cu/M=0.02, K/M=0.04, M=Zn+Fe) have been completed at 473 K, P_{CO}=150 kPa and varying H₂/CO ratios (2, 10 and 20). These were conducted in order to provide a better understanding of the behavior of Fe catalysts under varying H*/CO* surface coverages and also to provide a comparison with Co at the same conditions. CO rates increased with increasing H₂/CO ratios (0.45, 0.84 and 1.5 mol/h.g-at. Fe at H₂/CO ratio of 2, 10 and 20 respectively), suggesting a positive dependence of the rate on H* availability. CH₄ selectivities increased (from 1.3 to 4.5 to 6.8% upon increase in H₂/CO ratios from 2 to 10 to 20) and C₅₊ selectivities concurrently decreased (from 94% to 80% to 68%). An increase in H₂ concentration led to a decrease in the intrinsic termination to olefins, and the low molecular weight olefins did not undergo any secondary hydrogenation or readsorption reactions at any of the conditions tested.

In situ FTIR spectroscopic experiments were completed on a 12.7% Co/SiO₂ catalyst at 453 K and 473 K, 500 kPa, H₂/CO=2 in order to probe the autocatalytic effects of water on the reaction during this reporting period. The spectra collected in the absence of water showed bands corresponding to linearly adsorbed CO, formate, methylene and methyl groups and carbonates.

All these species were detected only when Co was present on the SiO₂ surface. The surface species corresponding to methylene, methyl, carbonates and formates were all spectator species. Upon addition of water, the CO adsorption band broadened and shifted to lower wavenumbers, indicating a weakening of the CO bond due to coordination with hydroxyl groups. Hydroxyls were also observed on SiO₂ upon water addition. The area under the CO adsorption band, which is an indication of the total number of CO molecules adsorbed, increased by ~15% upon addition of water. However, this effect was irreversible and the catalyst appeared to have altered its structure irreversibly upon the initial addition of water. Further addition of water did not bring about significant changes in the intensity of the CO band, indicating that the autocatalytic effect of water in promoting the FT rate cannot merely reflect as an increase in the number of CO adsorption sites.

Switching experiments have been started on Co/SiO₂ under FTS reactions during this quarter. These initial studies involved switches between synthesis gas and hydrogen at 464 K and 600 kPa (FT conditions) in order to quantify the number of active sites during the reaction. A computational method was developed to analyze the data recorded during the switch and to estimate the carbon coverage during the reaction. The percentage coverage of the catalytic sites by active carbon was estimated at 18% at low (5%) CO conversion. Analyses of the methane flow rate evolved after the switch show the presence of two different pools of adsorbed carbon on the surface during the reaction. Experiments at different bed residence time suggest that the coverage of the catalyst by carbon increases upon increasing the bed residence time.

Dr. Senzi Li will finish her appointment at Berkeley on 30th April 2001. Three manuscripts, describing the site requirements and the effect of promoters (K, Cu and Ru) on the

structure, reduction/carburization behavior and the catalytic performance of Fe- or Fe-Zn-based catalysts, have been prepared. The manuscript drafts are currently in the final stages of revision.

Dr. Peter Szedlacsek from the University of Otuos Lorand in Budapest, Hungary has joined the group in March and will devote about 50% of his time to this project. He will be continuing research on Fe-based FTS catalysts.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high- α catalysts.

See Task 2 for catalyst preparations.

Task 2. Catalyst Testing

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

A. Fischer-Tropsch Synthesis: Influence of Process Parameters on Productivity and Selectivity of Alkali-Metal Promoted Iron Catalysts

Introduction

The Fischer-Tropsch synthesis (FTS) process, which converts carbon monoxide and hydrogen to hydrocarbons and oxygenates, makes coal or natural gas a promising alternative to petroleum. The mechanism and kinetics of the FTS process have been investigated (1-8). The process can be simplified as the following two reactions:



Average molecular weight of the hydrocarbon products depends on reactions conditions and catalyst. When an iron catalyst is utilized in the FTS, a significant amount of carbon is consumed in the water gas shift (WGS) reaction, as shown by the second reaction. The complexity of the FTS process is the major obstacle in understanding the mechanism and defining the kinetics. A variety of proposals for the FTS mechanism are based on the surface species and various elementary reaction steps. Different kinetic equations were expressed in power-law based on the empirical data and the mechanism proposals from the literature (2).

Process parameters, i.e, reaction temperature, pressure and space velocity, have a significant influence on FTS kinetics, catalyst activity and selectivity. Due to the complexity of the FTS process, development of the FTS technology leads to the complications in the theoretical interpretation of the research data. A well designed experiment using statistic principles could sharply lower the cost of the experimental investigation. A common method to conduct the experiment is to change one factor at a time. Although it remains a conservative research approach, it is neither sufficient nor possible to detect the interactions between the factors involved. In this study, we investigate the effect of these process parameters, i.e., reaction temperature, pressure and space velocity, on carbon monoxide conversion and on carbon dioxide and methane selectivity. Experiments were conducted using 3-factor and 2-level factorial design approach. The influence of each factor on conversion and selectivity and on interactions between temperature, pressure and space velocity are discussed based on the experiments results.

Experimental

Preparation of Unpretreated Catalyst

Three iron catalysts promoted with potassium and beryllium were prepared and tested in this study. Table 1 gives the compositions of the catalysts used in this study. The ratios shown in Table 1 are all atomic ratios of iron to promoters. Precipitated iron catalysts were prepared with tetraethyl orthosilicate, iron nitrate, potassium carbonate and copper nitrate (9).

Copper is widely used as a promoter for iron FTS catalyst. It was believed that copper can facilitate the activation process. Copper can also minimize the sintering of iron catalysts by lowering the reduction temperature (5). In this study, the 100Fe/4.6Si catalyst base powder was impregnated with the proper amount of aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution to give an atomic composition of 100Fe/4.6Si/2.0Cu. The amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ added will depend on the

iron content of the base catalyst. In addition to copper, potassium is also an important promoter for an iron catalyst to improve the FTS activity and selectivity. Details of catalyst preparation was given elsewhere (9).

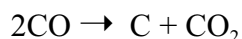
In-situ Activation of Unpretreated Catalysts

The iron catalyst needs to be activated with H₂, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (6,7). It was reported that catalysts activated with CO yielded higher long-chain hydrocarbons than syngas and H₂ activated catalysts. In addition, activation conditions may also influence the performance of the iron catalyst.

In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C, 1.2 MPa for 24 hours. The reduction of Fe₂O₃ with CO occurs in two steps:



In addition, CO₂ may be formed by the Boudouard reaction:



Previous work in our lab showed that approximately 50 % to 75% more carbon was present in the catalyst mass than was needed to form Fe₅C₂ (8). Gradual oxidation of Fe₅C₂ to Fe₃O₄ was observed when iron catalyst was used in FTS and a catalyst with long-term stability consists of a mixture of Fe₃O₄ and iron carbides.

Reactor System

A one-liter continuous stirred tank reactor (CSTR) was used in this study (Figure 1). A sintered-metal filter was installed to remove the wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap (200°C). A warm

trap (100°C) and cold trap (0°C) were used to collect oil, light wax and water samples. Tail gas from the cold trap was analyzed with an HP RGA GC.

A gas mixer fed with a CO and an H₂ stream fitted with mass controllers was used to provide a simulated synthesis gas. After the catalysts were activated with CO, syngas was introduced at a rate of 3.1 or 10 sl/hr/gram-catalyst. Reaction conditions were 230°C, 1.2 MPa and a stirrer speed of 750 rpm.

Product Sampling and Analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. Table 2 gives the summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. Vapor phase above the slurry phase passed to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC. Molar compositions of C₁-C₇ olefins and paraffins were thus obtained. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formulas:

$$CO \text{ Conversion} = \frac{N_{CO-in} - N_{CO-out}}{N_{CO-in}} \bullet 100\%$$

$$CH_4 \text{ Selectivity} = \frac{N_{CH_4-out}}{(N_{CO-in} - N_{CO-out} - N_{CO_2-out})} \bullet 100\%$$

$$CO_2 \text{ Selectivity} = \frac{N_{CO_2-out}}{(N_{CO-in} - N_{CO-out})} \cdot 100\%$$

where N is the molar flow rate in moles/hour.

The oil and light wax samples were mixed before analysis with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed with an HP5890 GC.

Results and Discussions

Experiment Design

The purpose of factorial experimental design is to limit the number of experiments required to investigate the influence of the factors involved in a process. By proper design of the experiment, it is also possible to study the interaction between the factors concerned. In this study, FTS reaction temperature, pressure and space velocity were studied as the factors that affect the results of conversion, productivity and selectivity. A higher temperature may yield a higher CO conversion, but it may also result in a higher undesired CO₂ and CH₄ selectivity. Studying the effect of each of these factors can lead to a better understanding of the process and in process design.

A process can be described by a mathematical expression as a function of factors x_1, x_2, x_3, \dots , i.e.

$$Y = f(x_1 + x_2 + x_3 + \dots)$$

This can be expressed with an approximate equation as follows:

$$Y = B_o + \sum_j B_j Z_j + \sum_{i < j} B_{ij} Z_i Z_j + \sum_j B_{jj} Z_j^2 + \dots$$

Two factorial experimental design can provide the maximum information from a minimum number of research trials (13). It is believed that two-level factorial design is the most effective, although three- or four-level design can detect the nonlinearity in functional relationships between the factors and the response variable. However, two-level experiments require much fewer trials than a three- or four-level design so that it is more cost effective to conduct several two-level experiments than the latter.

An eight-run experiment was designed based on the three factor and two-level factorial design, as shown in table 3. It is important that the actual experiment was conducted in a random order instead of the order listed in the table to ensure the integrity of the experiment. The low (-1) and high (+1) level pairs for temperature, pressure and space velocity were 230/270°C, 1.2/2.9 MPa and 5.0/10.0 sl/h/g-Fe, respectively. Figures 1 through 5 give the response variables of CO and H₂ conversion, hydrocarbon rate (g/h/g-Fe) and CO₂ and CH₄ selectivity for the reaction catalyzed with potassium and beryllium promoted iron catalysts.

The effect of a single factor is named as the “main effect” and that between any two factors named as “interaction.” While the main effect depicts the influence of a single factor, interaction effects describe the effect of one factor on the behavior of the other. Main effect is calculated by the following equation:

$$E_T = \text{average response at low level of factor T} - \text{average response at high level of factor T}$$

$$= \frac{(Y_{T_2P_1S_1} + Y_{T_2P_1S_2} + Y_{T_2P_2S_1} + Y_{T_2P_2S_2})}{4} - \frac{(Y_{T_1P_1S_1} + Y_{T_1P_1S_2} + Y_{T_1P_2S_1} + Y_{T_1P_2S_2})}{4}$$

where Y is the response variable, such as CO conversion, CO₂ selectivity or hydrocarbon rate; T, P and S are three factors defined in this study, i.e., temperature, pressure and space velocity. A

positive effect indicates the response variable changes in the same direction as the factor changes while a negative effect behaves the opposite.

Interaction effect between two factors is calculated in the same way:

I_{TP} = Effect of B at level 2 of Factor T - Effect of B at level 1 of Factor T

$$= \frac{(Y_{T_2P_2} - Y_{T_2P_1}) - (Y_{T_1P_2} - Y_{T_1P_1})}{2}$$

In case of a 3-factor experiment, interaction can also be calculated by substituting the four terms in the above equation as:

$$\begin{aligned} Y_{T_2P_2} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \\ Y_{T_2P_1} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \\ Y_{T_1P_2} &= \frac{1}{2} \bullet (Y_{T_1P_2S_1} + Y_{T_1P_2S_2}) \\ Y_{T_1P_1} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \end{aligned}$$

Carbon Monoxide and Hydrocarbon Conversion

Based on the concepts above, a factorial design and response scheme for each series of FTS reactions was designed as shown in Table 4. Table 5 shows the results of three series of experiments using two potassium and one beryllium promoted iron catalysts. It is shown in Table 5 and Figure 1 that reaction temperature produced the largest effect on CO conversion when K1.44 (Fe:K = 100:1.44) catalyst was used. When temperature changed from 230 to 270°C, average CO conversion increased by 26.77%. A much smaller effect of 6.64% was caused by pressure as observed from the experiment. Space velocity (Factor S) generated a negative effect on CO conversion; therefore, conversion decreased as the space velocity increased. Interactions between pressure and space velocity and the three-factor interaction were

insignificant (<1%). Because a larger normal experimental error is expected, the two interaction effect (PS and TPS) can be neglected. The interaction between temperature and space velocity, and that between temperature and pressure were found to only 5 to 8%, respectively. Reaction over K5.00 (Fe:K = 100:5) catalyst showed a similar results as indicated in both Table 5 and Figure 1. Temperature effect was as high as 31.08% and space velocity 20.70% while the effect of pressure and interactions of PS and TPS showed insignificant values (1-3%).

Hydrogen conversion showed a similar behavior to CO conversion for FTS reaction over both potassium promoted iron catalysts. For both catalysts, temperature yielded an effect (24.99-26.85%) greater than that of space velocity (12.63-22.40%) on H₂ conversions. Pressure effect showed an even smaller effect on potassium promoted catalysts. All interaction effects were below 6%, which were much less important than the single main effect.

Beryllium catalyzed reactions yielded a different behavior as indicated in Table 5. When Be1.44 (Fe:Be = 100:1.44) catalyst was used, the temperature effect was much smaller than that over potassium promoted catalysts. The effects of pressure and space velocity were equivalent to those over potassium promoted catalysts. Interaction between temperature and pressure was much greater than the main effect of each factor. All other four interactions showed a negligible value. The different behavior over Be promoted catalyst from that over potassium catalysts was also shown in Figures 1 and 2. When pressure increased from 1.2 to 2.9 MPa at the lower level of temperature (230°C), both H₂ and CO conversions increased from 20% to 80%. At high level of temperature (270°C), however, an increase in pressure showed a decrease in CO and H₂ conversions, suggesting that there is a considerable interaction effect between temperature and pressure in the process.

Figures 1 and 2 also show that the highest CO and H₂ conversions over potassium catalysts were obtained at high level of temperature and low level of space velocity. Pressure did not show an important role in CO and H₂ conversions as shown in Table 5 and Figures 1 and 2. Beryllium promoted catalyst, however, showed the highest conversions at a low temperature (230°C) and a lower pressure (1.2 MPa).

Methane Selectivity

Methane selectivity for potassium promoted catalysts was appreciably affected by temperature only. Neither pressure nor space velocity played an important role in methane selectivity. All interaction effects except that between temperature and pressure were insignificant. Average CH₄ selectivity at the low temperature level (230°C) was 0.54 and 1.94% at 270°C. A pressure increase from 1.2 to 2.9 MPa raised the CH₄ selectivity from 0.98 to 1.5% while an increase in space velocity showed little change in CH₄ selectivity. Interaction of temperature and pressure showed a value of -0.563% and the results in Table 5 revealed a negligible level of interactions between other factors. The FTS reaction over K5.0 catalyst showed similar results and showed a slightly lower effect of temperature and interaction between temperature and pressure. When temperature level changed from 230 to 270°C, CH₄ selectivity increased from 0.96 to 1.85%, which is the largest main effect among all three factors. Similar to K1.44 catalyst, K5.0 catalyst also revealed an interaction effect between temperature and pressure of 0.29%, which is the only appreciable value among all interactions. Beryllium promoted catalyst, however, showed a greater effect of pressure (1.29%) than that of temperature (1.14%). Space velocity did not have an important effect on CH₄ selectivity with this catalyst, which is similar to potassium promoted catalysts. All interaction effects except those of three-factor effects showed a larger value than the main effect of pressure and temperature.

Figure 3 shows that the overall CH₄ selectivity of FTS over the Be promoted catalyst was much higher than for the potassium promoted catalysts. The change in selectivity over Be promoted catalyst was much larger than that over potassium promoted catalyst (Figure 3). Lower temperature yielded lesser CH₄ than that at a higher temperature 0314 and higher pressure raised the CH₄ production slightly. A CH₄ selectivity of 0-1.13% was observed at 230°C and 1.65-2.10% at 270°C as shown in Figure 3. Beryllium promoted catalyst yielded a CH₄ selectivity as high as 15.02% at 270°C and as low as 5.07% at 230°C, suggesting that Be is not a good promoter in terms of CH₄ selectivity.

Carbon Dioxide Selectivity

For all three catalysts, temperature had a more important effect on CO₂ selectivity than pressure and space velocity. All interaction effects over potassium promoted catalysts were not appreciable while FTS over Be promoted catalyst showed significant interactions between all factor pairs. As shown in Table 5, a temperature change from 230 to 270°C over K1.44 catalyst resulted in an average CO₂ selectivity increase from 19.20 to 38.5%. When the K5.0 catalyst was utilized, a temperature increase resulted in a CO₂ increase from 27.13 to 43.3%. Pressure effect over potassium promoted catalysts, however, showed a much less important effect than that of temperature. A decrease from 29.65 to 28.06% over K1.44 catalyst and that from 38.81 to 31.64% were observed when pressure changed from 1.2 to 2.9 MPa. Similarly, decreases in CO₂ selectivity from 31.60 to 26.11% over K1.44 catalyst and from 38.09 to 32.36% over K5.0 catalyst were found when the space velocity increase from 5.0 to 10.0 sl/h/g-Fe.

Results from beryllium promoted catalyst showed that among all three factors, temperature played the most important role. When temperature changed from 230 to 270°C, CO₂ selectivity increase from 39.04 to 45.90%. The other two factors, pressure and space velocity,

however, showed a change of 2.35 and 2.59 in CO₂ selectivity. Interactions between all factor pairs except that between temperature and pressure were not negligible.

Figure 4 indicates that overall CO₂ selectivity over Be1.44 catalyst was higher than that over potassium promoted catalysts. Beryllium promoted catalyst yielded as high as 50% CO₂ and the lowest CO₂ of 23.82% over K1.44 catalyst was obtained at 230°C, 2.9 MPa and 10 sl/h/g-Fe. The figure also shows that K1.44 catalyst produced slightly lower CO₂ under all conditions. The lowest CO₂ selectivity of ~16% over the two potassium promoted catalysts was obtained at 230°C, 1.2 MPa and 10 sl/h/g-Fe.

Hydrocarbon Rate

Similar to all other effects, temperature had the most important influence on hydrocarbon rate. As shown in Table 5, a temperature change from 230 to 270°C resulted in an increase in hydrocarbon rate from 0.14 to 0.54 g/h/g-Fe over K1.44 catalyst and from 0.39 to 0.72 g/h/g-Fe over K 5.0 catalyst. Pressure and space velocity, however, affected the hydrocarbon rate to a much less extent, ranging from 0.04 to 0.14 g/h/g-Fe when potassium promoted catalysts were utilized. It is also found from Table 5 that the effect of pressure was greater than that of space velocity when K1.44 catalyst was used while the opposite result was observed when the K 5.0 catalyst was used. All interaction effects were insignificant when potassium promoted catalysts were used.

When Be was used, temperature effect was equivalent to that of pressure and space velocity. Temperature, pressure and space velocity generated an effect of -0.16, 0.18 and 0.22 g/h/g-Fe, respectively, indicating that space velocity had a larger effect than pressure and temperature. The interaction between temperature and pressure showed a significant value while all other interactions did not indicate an appreciable values.

Figure 5 shows that Be behaved differently from potassium and the highest hydrocarbon rate of 1.52 g/h/g-Fe was observed at 230°C, 1.2 MPa and 10 sl/h/g-Fe when Be1.44 catalyst was used. Under these conditions, Be yielded a higher hydrocarbon rate than potassium. The catalyst promoted with 5% potassium showed a higher overall hydrocarbon rate than that the 1.44% potassium catalyst. The highest hydrocarbon of 0.73 g/h/g-Fe was found at 270°C, 1.2 MPa and 10 sl/h/g-Fe when K1.44 catalyst was utilized and 0.85 g/h/g-Fe at 270°C, 2.9 MPa and 10 sl/h/g-Fe when K5.0 catalyst was used.

Conclusions

Factorial design is an effective approach for studying process parameters. By designing the experiment, the number of trials was minimized and the cost and time were significantly saved. Although two-level factorial design failed to detect the nonlinearity of the process between the high and low level of factors concerned, it is still the more effective way to conduct several two-level experiments than to perform a series of experiment of three- or four-level. In addition, two-level factorial design reveals the interactions between factors.

Results from this study shows that temperature had the most important influence on CO and H₂ conversions, CO₂ and CH₄ selectivity and hydrocarbon production rate in FTS process. Pressure and space velocity played a less significant role in affecting FTS CO and H₂ conversions. Interaction effects of temperature and pressure from beryllium promoted catalyst was significant. A temperature increase from 230 to 270°C significantly raised the CO conversion from ~19 to 35% when potassium promoted catalysts were utilized. Hydrogen conversion was also significantly increased for temperature increase. An increase in temperature from 230 to 270°C resulted in an H₂ conversion increase of 25-27%. Temperature effect on H₂ conversion using Be promoted catalyst was not as important as that using potassium promoted

catalysts. Pressure and space velocity effects were found to be much less important than temperature. Only a 2.4 to 6.6% change in CO conversion was found as pressure increased from 1.2 to 2.9 MPa when potassium promoted catalysts were used. Space velocity had a slightly greater effect on CO conversion than pressure and a 13 to 20% increase in CO conversion was found when space velocity was changed from 5 to 10 sl/h/g-Fe.

It is also found that when potassium promoted catalysts were utilized, CH₄ selectivity was not significantly affected by any of these three factors. Temperature had the more important effect on CH₄ selectivity than that of pressure and space velocity. Carbon dioxide selectivity, however, changed more appreciably with the change in reaction temperature. A 16.2 to 19.3% increase in CO₂ was found when temperature was increased from 230 to 270°C when potassium promoted catalysts were used. Pressure and space velocity did not yield an important influence on CO₂ selectivity.

Acknowledgment

This work was supported by U.S. DOE contract number DE-FC26-98FT40308 and the Commonwealth of Kentucky.

Nomenclature

- Y Response variable
- E Main effect of a factor
- I Interaction between factors

Subscribe

- T Reaction temperature
- P Reaction pressure
- S Space velocity
- T1 Temperature at low level
- T2 Temperature at high level
- P1 Pressure at low level
- P2 Pressure at high level
- S1 Space velocity at lower level
- S2 Space velocity at high level

References

1. M.E. Dry. *Appl. Catal. A* 138 (1996).
2. G.P. Van der Laan and A.A.C.M. Beenackers. *Catal. Rev.-Sci. Eng.* 41 (1999).
3. Ajoy P. Raje and Burtron H. Davis. *Catalysis Today*, Volume 36, Issue 3, 6 June 1997.
4. A.A. Adesina. *Appl. Catal. A* 138 (1996).
5. M.E. Dry, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis-Science and Technology*, Vol. 1, Springer, New York (1981).
6. W.H. Zimmerman and D.B. Bukur. *Can. J. Chem. Eng.* 68 (1990).
7. F.H. Ribeiro, A.E. Schach von Wittenau, C.H. Bartholomew and G.A. Somorjai. *Catal. Rev.-Sci. Eng.* 39 (1997).
8. J.P. Hindermann, G.J. Hutchings and A. Kiennemann. *Catal. Rev.-Sci. Eng.* 35 (1993).
9. Mingsheng Luo and Burtron H. Davis. *Appl. Catal. A*, submitted.
10. D. B. Bukur, L. Nowichi and X. Lang, *Energy and Fuels*, 9, 620 (1995).
11. R. J. O'Brien, L. Xu, R. L. Spicer and B. H. Davis, *Energy and Fuels*, 10,921-926(1996).
12. R. J. O'Brien, Y. Zhang, H. H. Hamdeh, B. H. Davis, "Mossbauer study of precipitated unpromoted iron Fischer-Tropsch catalyst," Preprints, 44(1) ACS, Division of Petroleum Chemistry, Mar. 21-25, Anaheim, CA, 100-102, (1999).
13. Virgil L. Anderson. *Design of Experiments II*, Marcel Dekker, Inc., New York (1974).
1. Robert H. Lochner, in *Quality planning, control, and improvement in research and development*, edited by George W. Robert, Marcel Dekker, Inc, New York (1994).

Table 1

Alkali Promoted Catalysts used in this Study^a

Catalyst ID	Fe	Si	Cu	K	Be	Catalyst Loading (g) ^b
Be 1.44	100	4.6	---	---	1.44	5.00
K 1.44	100	4.6	2.0	1.44	---	9.59
K 5.00	100	4.6	2.0	5.00	---	32.20

a. Atomic ratio.

b. Grams catalyst in 300 g start-up oil.

Table 2		
Analyzers for FTS Products		
Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5890 GC	Water	FID
HP 5790A GC	Oil + Light Wax	TCD
HP 5890 Series II Plus	Heavy Wax	FID

Table 3

Three-Factor and Two-Level Factorial Experiment Plan

Run ID	Temperature (°C)	Pressure ^a (MPa)	Space Velocity (sl/h/g-Fe)
A	230	1.2	5
B	230	1.2	10
C	230	2.9	5
D	230	2.9	10
E	270	1.2	5
F	270	1.2	10
G	270	2.9	5
H	270	2.9	10

a. Gauge pressure.

Table 4

Experiment Design and Response Scheme for CO Conversion Study with K 1.44 Catalyst

Standard Run Order	Actual Run Order	Response (CO Conversion)	Temperature		Pressure ^a		Space Velocity	
			Factor T		Factor P		Factor S	
			Level	(°C)	Level	(MPa)	Level	(sl/h/g-Fe)
A	3	21.63	-1	230	-1	1.2	-1	5
B	8	15.85	-1	230	-1	1.2	+1	10
C	1	22.08	-1	230	+1	2.9	-1	5
D	6	17.29	-1	230	+1	2.9	+1	10
E	5	49.38	+1	270	-1	1.2	-1	5
F	7	30.27	+1	270	-1	1.2	+1	10
G	4	63.21	+1	270	+1	2.9	-1	5
H	2	21.09	+1	270	+1	2.9	+1	10

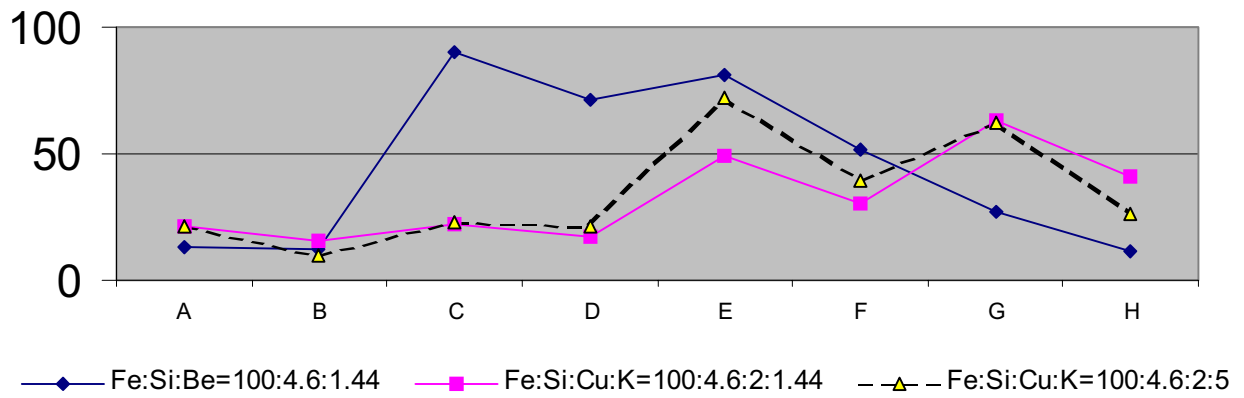
a. Gauge pressure.

Table 5

Summary of Effect Analysis from Three-Factor Two-Level Experiment Design

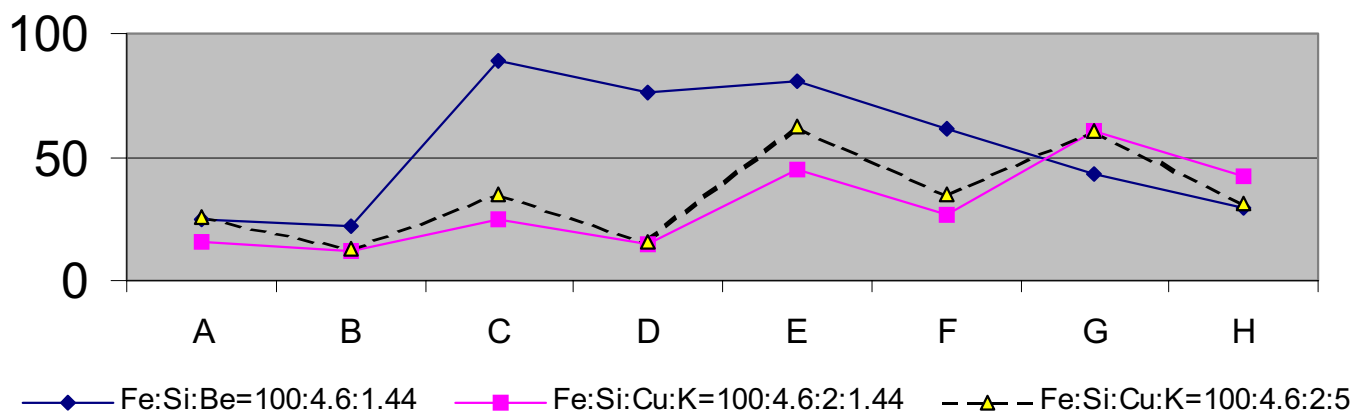
Response Variable	Catalyst ID	Average Response	Factor T (°C)	Factor P (MPa)	Factor S (sl/h/g-Fe)	Interaction TP	Interaction TS	Interaction PS	Interaction TPS
CO Conversion	K 1.44	32.60	26.77	6.64	-12.95	5.69	-7.67	-0.51	-1.00
	K 5.00	34.46	31.08	-2.38	-20.70	-8.78	-13.96	1.61	-3.07
	Be 1.44	44.74	-4.15	10.44	-15.92	-57.32	-6.56	-0.75	8.02
H ₂ Conversion	K 1.44	30.14	26.85	10.69	-12.63	4.83	-5.66	-1.83	1.22
	K 5.00	34.84	24.99	1.48	-22.40	-4.26	-6.15	-2.05	1.70
	Be 1.44	53.35	0.69	12.02	-12.12	-47.15	-4.18	-1.29	3.87
CH ₄ Selectivity	K 1.44	1.24	1.39	0.52	0.01	-0.56	0.05	-0.08	-0.03
	K 5.00	1.40	0.89	0.07	-0.04	0.29	-0.02	-0.11	0.01
	Be 1.44	8.99	1.14	1.29	0.77	1.59	3.40	4.12	-0.25
CO ₂ Selectivity	K 1.44	28.85	19.30	-1.59	-5.48	0.60	-0.53	-0.18	-1.26
	K 5.00	35.22	16.2	-7.18	-5.74	4.62	0.44	-3.17	0.43
	Be 1.44	42.45	6.82	2.59	-2.35	-2.24	7.31	11.07	-4.88
Hydrocarbon Rate	K 1.44	0.34	0.41	0.14	0.06	0.08	0.04	0.03	0.04
	K 5.00	0.55	0.34	0.04	0.11	-0.20	-0.07	0.06	-0.12
	Be 1.44	0.69	-0.16	0.18	0.22	-0.87	-0.14	-0.03	-0.14

Figure 1. CO Conversion



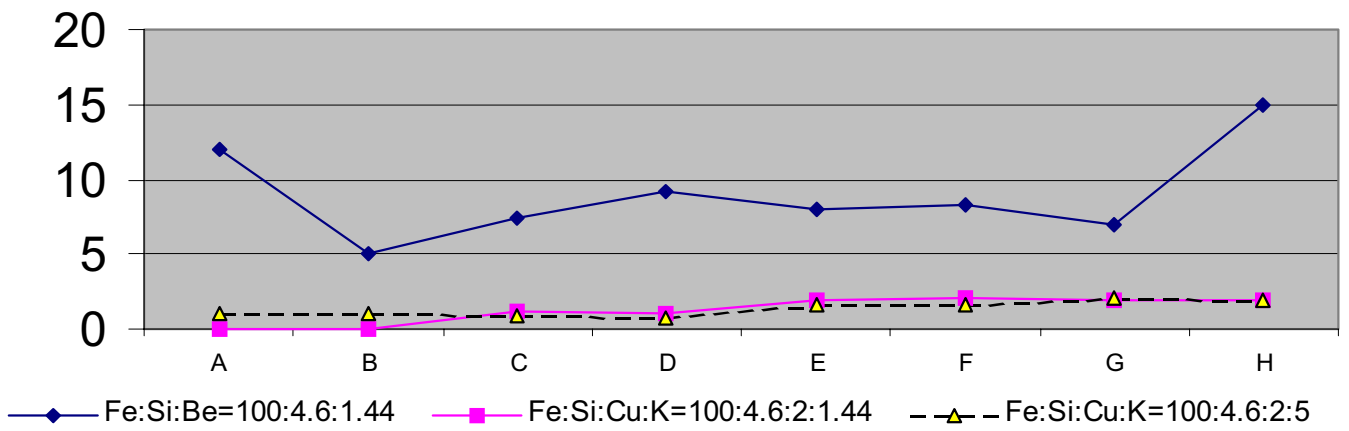
A: 230°C, 425psig, 5sl/h/g; B: 230°C, 425psig, 10sl/h/g;
C: 230°C, 175psig, 5sl/h/g; D: 230°C, 175psig, 10sl/h/g
E: 270°C, 425psig, 5sl/h/g; F: 270°C, 425psig, 10sl/h/g;
G: 270°C, 175psig, 5sl/h/g; H: 270°C, 175psig, 10sl/h/g

Figure 2. H₂ Conversion



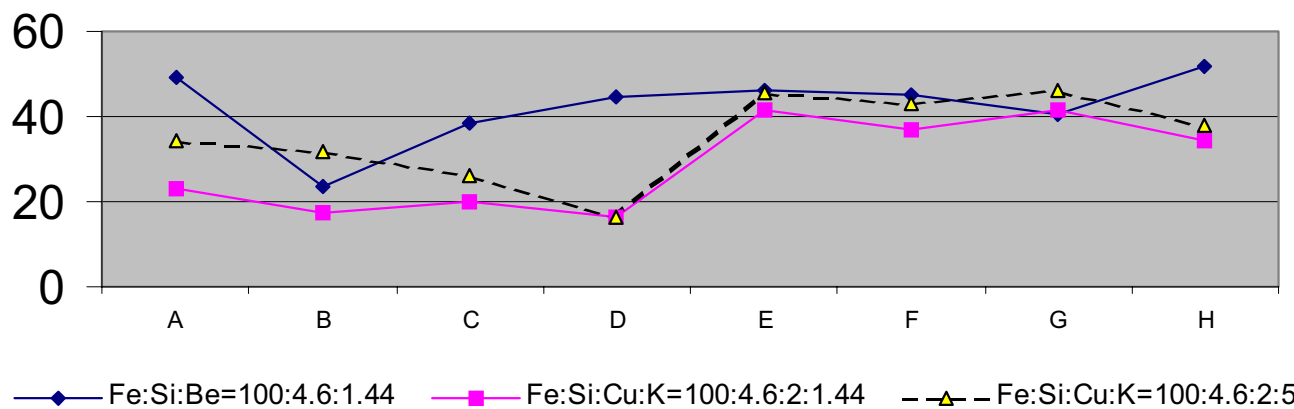
A: 230°C, 425psig, 5sl/h/g; B: 230°C, 425psig, 10sl/h/g;
C: 230°C, 175psig, 5sl/h/g; D: 230°C, 175psig, 10sl/h/g
E: 270°C, 425psig, 5sl/h/g; F: 270°C, 425psig, 10sl/h/g;
G: 270°C, 175psig, 5sl/h/g; H: 270°C, 175psig, 10sl/h/g

Figure 3. Methane selectivity



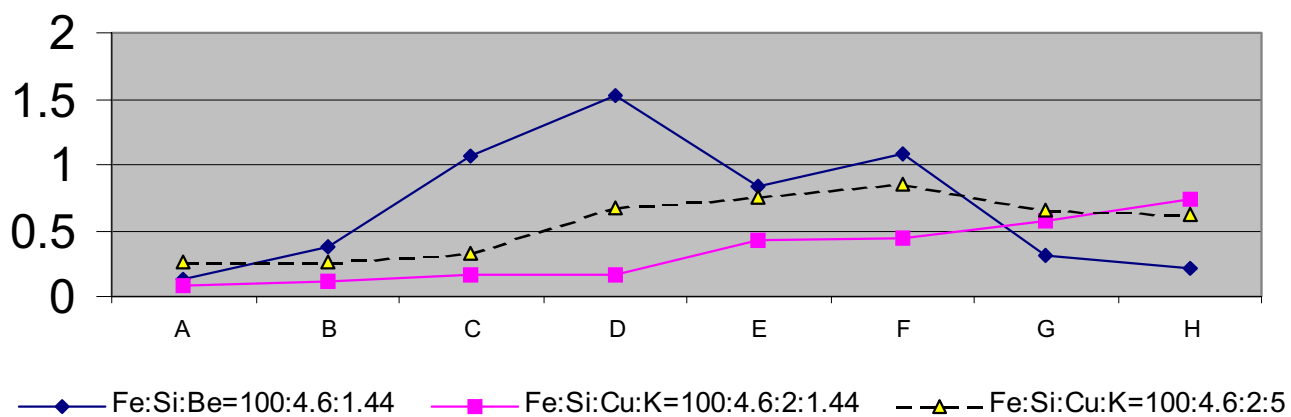
A: 230°C, 425psig, 5sl/h/g; B: 230°C, 425psig, 10sl/h/g;
C: 230°C, 175psig, 5sl/h/g; D: 230°C, 175psig, 10sl/h/g
E: 270°C, 425psig, 5sl/h/g; F: 270°C, 425psig, 10sl/h/g;
G: 270°C, 175psig, 5sl/h/g; H: 270°C, 175psig, 10sl/h/g

Figure 4. CO₂ Selectivity



A: 230°C, 425psig, 5sl/h/g; B: 230°C, 425psig, 10sl/h/g;
C: 230°C, 175psig, 5sl/h/g; D: 230°C, 175psig, 10sl/h/g
E: 270°C, 425psig, 5sl/h/g; F: 270°C, 425psig, 10sl/h/g;
G: 270°C, 175psig, 5sl/h/g; H: 270°C, 175psig, 10sl/h/g

Figure 5. Hydrocarbon rate



A: 230°C, 425psig, 5sl/h/g; B: 230°C, 425psig, 10sl/h/g;
C: 230°C, 175psig, 5sl/h/g; D: 230°C, 175psig, 10sl/h/g
E: 270°C, 425psig, 5sl/h/g; F: 270°C, 425psig, 10sl/h/g;
G: 270°C, 175psig, 5sl/h/g; H: 270°C, 175psig, 10sl/h/g