

## Executive Summary

### CAER

Promoted iron FTS catalysts showed a significant increase in CO conversion up to about K:Fe ratio of 5:100. An increase in K loading (K/Fe = 0.0144 to 0.020) increased the alpha value from 0.71 to 0.85; a further increase to K/Fe = 0.050 increased the alpha value to 0.91.

Catalysts with different potassium loadings showed different lengths of induction, in which the FTS reaction showed increasing conversion from a low initial value to a peak value before declining to a stable activity level. Lower potassium loadings produced a higher maximum conversion and a shorter induction period. Although the induction period and the peak conversion values were dependent of the K loading, the stabilized conversions and the stabilization period were independent of potassium content. All three of the higher level potassium promoted catalysts yielded a stabilized hydrogen conversion at about 400 hours of total on-stream time.

An increase in potassium content to 5:100 = K:Fe substantially enhanced the long-chain hydrocarbon yield with a concurrent decrease in the gas fraction (C<sub>1</sub>-C<sub>4</sub>) by nearly 50% and the gasoline(C<sub>5</sub>-C<sub>11</sub>) fraction by over 40%. Further increase in potassium iron ratio from K/Fe = 0.075 to 0.10 did not further enhance the production of the heavy fraction. Similar to the CO conversion profile, CO<sub>2</sub> selectivity also shows an induction period. The CO<sub>2</sub> selectivity for all three catalysts went through a rapid increase during the initial period and then declined from its peak value of 42% to a stable level of 39%. Potassium had little effect on CO<sub>2</sub> selectivity for K/Fe ratios in the range of 5:100 to 10:100 for the potassium promoted catalysts. Methane selectivity declined gradually during the first 250 hours of run. All three higher potassium-containing catalysts yielded a stable methane selectivity of 1.5% after the first 250 hours of run. The surface structure and/or composition changes in the first 250 hours of reaction favor the

formation of CO<sub>2</sub> but inhibit the formation of methane. All three potassium promoted catalysts yielded a stable CO<sub>2</sub> selectivity of 38-39% and methane 1.5%.

Increase in reaction temperature resulted in a new induction period and a new higher activity than before the reaction temperature was increased. In addition to reaction temperature and pressure, H<sub>2</sub>:CO ratio also had an important influence on FTS conversions. Increase of the H<sub>2</sub>:CO ratio in the feedstock gas lowered the H<sub>2</sub> utilization rate. Higher H<sub>2</sub>:CO ratio feedstock gas lowered the FTS catalyst activity due to the lower iron carbide formation rate than that when a low H<sub>2</sub>:CO ratio gas was used. CO<sub>2</sub> selectivity decreased immediately after the H<sub>2</sub>:CO ratio increased, suggesting that water gas shift reaction be inhibited due to the higher H<sub>2</sub> content in the gas of H<sub>2</sub>:CO ratio of 1.7.

Iron FTS catalysts promoted with group II alkali metals produced lower CO conversions than potassium. Among the four group II alkalis, magnesium yielded the highest and calcium the lowest conversion. Beryllium and barium promoted iron catalysts, however, showed a better stability than any other group II alkalis and potassium promoted catalysts based on the results of over 500 hours of FTS reactions.

Potassium also generated the highest CO<sub>2</sub> and hydrocarbon rates but the lowest water rate, suggesting that potassium possesses higher water gas shift and FTS activities than group II alkali metals. Among the group II alkalis, barium produced the lowest water yield but the highest CO<sub>2</sub> yield; therefore, the highest water gas shift activity was obtained from Ba promoted catalysts. All group II alkalis generated similar hydrocarbon, CO<sub>2</sub> and methane rates. It was also found that group II alkalis produced a similar oxygenate rate, except that Ba yielded a higher ethanol and Mg higher normal propanol than other group II alkali metals. The olefin ratio, however, did not reveal any difference among group II alkalis and potassium.

FTS production distributions indicate that potassium generated the higher diesel ( $C_{12}$ - $C_{18}$ ) and heavier ( $C_{19+}$ ) fraction as well as lower gaseous ( $C_1$ - $C_4$ ) and gasoline ( $C_5$ - $C_{11}$ ) fractions than group II alkalis. All alkalis yielded the same hydrocarbon rate except that potassium showed a higher hydrocarbon rate than group II alkalis at a medium space time.

Among the group II alkalis, beryllium produced the highest methane, ( $C_2$ - $C_4$ ) and gasoline fractions. All group II alkalis yielded a similar diesel fraction but magnesium and calcium produced lower heavy fractions ( $C_{19+}$ ) than beryllium and barium. At a low space time, potassium generated a lower methane selectivity than group II alkalis. At a relatively high space time, potassium produced a similar methane selectivity as calcium, magnesium and beryllium. Barium yielded a higher methane selectivity than any other alkalis at a high space time. Potassium generated a slightly higher alpha value than the group II alkalis but there was little difference in alpha values among all group II alkalis catalyzed FTS reactions.

Carbon dioxide selectivity, water and  $CO_2$  partial pressure results indicate that potassium possesses a better water gas shift activity than any group II alkali. Barium generated the highest WGS activity among the group II alkalis while magnesium showed the lowest. Higher WGS activity for potassium promoted catalysts may cause a lower carbon utilization rate than for Group II alkalis because an appreciable amount of CO was consumed in the WGS reaction.

TPR and  $H_2$  chemisorption with pulse reoxidation were used to study the reducibility of cobalt Fischer-Tropsch catalysts. Different supports (e.g.,  $Al_2O_3$ ,  $TiO_2$ ,  $SiO_2$ , and  $ZrO_2$  modified  $SiO_2$ ) and a variety of promoters, including noble metals and metal cations, were screened. Addition of Ru and Pt provided a similar effect by decreasing the reduction temperature of  $Co_3O_4$  and for CoO species where a significant CoO-support interaction was present, while Re mainly catalyzed the reduction of CoO. A slight decrease in cluster size was evidenced in  $H_2$  chemisorption/pulse reoxidation with noble metal promotion for catalysts reduced at the same

temperature, indicating that smaller Co oxide species that interacts with the support were reduced with the aid of the promoter. Increasing the cobalt loading, and therefore the average Co cluster size, was found to exhibit improved reducibility, by decreasing interactions with the supports. Addition of metal oxides such as B, La, K, and Zr were found to decrease the cobalt cluster size, and caused reduction to shift to higher temperatures.

A shakedown experimental run of the CAER's enhanced SBCR was successfully completed. SBCR gas holdup ( $\epsilon_g$ ), was measured by recording the liquid level in the overhead separation vessel at various superficial velocities through the reactor. Automatic control of the slurry level was both robust and effective in maintaining a constant catalyst inventory in the reactor. Differential pressure fluctuations from the level controller provided qualitative information regarding the slurry recirculation rate. The catalyst slurry filter yielded a clean wax product with virtually no signs of media plugging during 400+ hours of continuous operation.

Measured deactivation rates in the enhanced SBCR system were comparable to that of CSTR experiments under similar conditions. Transient problems with a previous SBCR run were identified and corrected. Another series of pilot plant runs are scheduled starting January 2001. Future experimental work with SBCR will focus on high alpha catalysts, wax filter media and catalyst attrition studies.

#### UC/B

In this reporting period, the research effort emphasized the preparation of manuscripts. A paper entitled "*The Structure and Site Requirements for Cu and K-promoted Fe-based Fischer-Tropsch Synthesis Catalysts*" was given at the 2000 annual meeting of the American Institute of Chemical Engineering, which was held at Los Angeles CA, from November 12-17. Two other abstracts (see appendix) have been submitted to international catalysis conferences and both talks have been accepted for oral presentation. A paper titled "*Structural Evolution and Site*

*Requirements for Fischer-Tropsch Synthesis Catalysts Based on Fe Oxide Precursors Promoted with Cu, Ru, or K*” has been accepted for presentation at the North American Catalysis Society meeting to be held in Toronto from June 3-8, 2001. A paper titled “*Fischer-Tropsch Synthesis Catalysts Based on Fe Oxide Precursors Modified by Cu and K: Structure and Site Requirements*” has been accepted for presentation at the 6<sup>th</sup> Natural Gas Conversion Symposium to be held at Alaska from June 16-19, 2001. The revisions of the latter paper have been completed and the paper has been accepted for publication in the Studies of Surface Science and Catalysis.

Two other manuscripts have been finished and submitted to journals. The manuscript entitled “*Structure and Site Evolution of Iron Oxide Catalyst Precursors during the Fischer-Tropsch Synthesis*” has been submitted to the Journal of Physical Chemistry B. The manuscript entitled “*Structural Analysis of Unpromoted Fe-Based Fischer-Tropsch Catalysts Using X-Ray Absorption Spectroscopy*”, which describes the joint work with the Center for Applied Energy Research (CAER) at the University of Kentucky, was submitted to Applied Catalysis A: General.

We have started the preparation of a new series of K- and Cu-promoted Fe-Zn oxide precursors under a different treatment protocol as our continuous effort to increase the surface area and the number of sites in Fe catalysts. Our previous studies have shown that higher surface area catalyst precursors tend to have higher surface area Fe carbides; the resulting Fe carbides, in turn, lead to higher FTS rates. In our last quarterly report (24), we have successfully prepared high surface area Fe-Zn oxide precursors using a newly developed alcohol-wash method. As the surface area of catalyst precursors increases, the substantial amount of water that is introduced to the catalyst precursors from the subsequent impregnation becomes the major cause of the decrease of the surface area during second dryings. Therefore, we minimized the water effect by dissolving  $K_2CO_3$  and  $Cu(NO_3)_2$  in the least amount of water and diluted the solution to the

volume needed for incipient wetness impregnation. A larger amount of K (K/Fe=0.02-0.08) and Cu (Cu/Fe=0.02-0.04) was doped to Fe-Zn oxide precursors to match their increased surface areas and to maintain a constant surface density of the components.

During this reporting period, FTS reactions were conducted with a Fe-Zn-Ru-K sample that was calcined at 673 K and compared with an identical sample calcined at 623 K that had been studied previously. A change in calcination temperature showed no differences in CO conversion and FT rates.

Experiments to study the effect of addition of  $^{13}\text{CO}_2$  to syngas on the FT rate and the product selectivity, which are aimed at getting further insight into the FTS reaction mechanism were delayed due to a problem with the GC-MS used for off-line analysis, which has since been fixed.

Switching experiments have also been started on Co/SiO<sub>2</sub> under FTS reactions during this quarter. The initial studies involved a switch between methane and synthesis gas at 473 K and 5 bar in an empty reactor. The transient output was almost identical to the step input. Such experiments will be conducted with the catalyst on-stream and these are expected to provide information regarding the number of active sites during the reaction.

Collection of *in situ* FTIR spectra on a Co/SiO<sub>2</sub> sample under reaction conditions has also been initiated. These experiments are being conducted both in the presence and absence of water and will provide insight on the autocatalytic behavior of water.

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

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

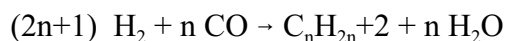
### **A. High Alpha Fischer-Tropsch Synthesis over Potassium Promoted Fe Catalysts**

#### **Abstract**

Iron Fischer-Tropsch synthesis (FTS) catalysts with different potassium loadings showed different induction periods during which the conversion increased from a low initial level to a peak value before declining to attain a lower activity that was stable at the reaction conditions. A lower K loading produced a higher peak conversion and a shorter induction period. Although the induction period and the peak conversion were slightly dependent on the K loading for the iron catalyst, the stabilized conversions and the stabilization periods were independent of potassium content. The C<sub>2</sub>-C<sub>4</sub> olefin to paraffin ratio of the gaseous products and the CO<sub>2</sub> selectivity did not change significantly as the potassium content increased from 5 to 10%. An increase in reaction temperature produced a new induction period and a higher conversion than that before the reaction temperature was increased. The H<sub>2</sub>:CO ratio also had an important influence on FTS conversions. Increasing the H<sub>2</sub>:CO ratio in the feed gas lowered the H<sub>2</sub> utilization. A higher H<sub>2</sub>:CO ratio feedstock gas produced lower FTS catalyst activity compared to a low H<sub>2</sub>:CO ratio gas.

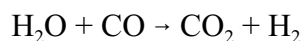
## Introduction

In a FTS process, the hydrocarbon is produced from CO and H<sub>2</sub> by a reaction which can be expressed as



where the average value of n is defined as  $\bar{n} = 1/(1-\alpha)$  or it can be rearranged as  $\alpha = 1 - (1/\bar{n})$

where  $\alpha$  is the ratio of chain termination to chain propagation (1). When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This side reaction consumes CO and water formed by the FTS reaction and produces additional hydrogen and carbon dioxide.



Potassium has long been used as a promoter for iron catalysts. It provides an increase in the alkene yield and a decrease in the CH<sub>4</sub> selectivity (2,3). Potassium can also increase the catalytic activity for FTS and water-gas shift (WGS) reactions (4). Low alpha FTS with iron catalysts that are similar, except they contain less than 2% of potassium than those used in this study, have been described earlier (5).

Dry reported the effect of K<sub>2</sub>O on iron catalysts utilized in a fixed bed and a fluidized bed reactor that operated at different temperatures (3) and according to Dry, the low temperature Fischer-Tropsch synthesis activity decreased as the loading of K<sub>2</sub>O increased while the high temperature reaction showed the opposite effect. As shown in Figure 1, at 200°C, the relative catalyst activity decreased from 64 to 29 when the relative K<sub>2</sub>O content increased from 0 to 2.6. At 330°C, the catalytic activities first increased and then stabilized at a certain level as the relative K<sub>2</sub>O content was above 2 to 3. For use at high temperature conditions, Figure 1 indicates



that the catalytic activity can be enhanced by potassium when its loading was lower than 3%, but a further increase in  $K_2O$  loading does not enhance the iron catalytic activity.

The influence of potassium on iron catalysts has been investigated by other researchers (e.g., 6-8). It is believed that strong bases of Group I metals have significant effects on both FTS activity and product selectivity. As the most effective promoter, potassium salts are widely used in iron catalysts; however, the readiness to form an alkali compound with common catalyst supports, such as alumina or silica, complicates the situation.

Although potassium enhanced the FTS activity and heavy fraction product distribution, high potassium loadings may cover too large of a fraction of the surface of the iron catalyst, resulting in a limited promotion effect or even a decrease in FTS conversions. In our study, a potassium loading higher than about 5.0% failed to further enhance the CO conversion.

Bonzel and Kerbs (9) claimed that potassium lowered the methane formation rate and increased the carbon deposition rate. It was also found that the deposited carbon was covered by potassium compounds rather than carbon sitting on top of the promoter. Huang et al. (6) studied the potassium promoted iron catalysts with XPS and found that two-thirds of the catalyst surface was covered by  $K_2O$  and  $SiO_2$ . Wang, et al. (7) applied the temperature programmed reduction (TPR) technique to study the effects of potassium. They suggested that potassium facilitates the desorption process of carbon monoxide and strengthens the Fe-C bond. Thus, potassium enhanced the selectivity of long-chain products, i.e., it resulted in a high alpha product distribution.

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 (3).

## Experimental

### Preparation of Catalyst

In this study, catalysts promoted with atomic ratios of 5, 7.5 and 10 potassium, based on 100 Fe, were used to produce high-alpha FTS products.

Precipitated iron catalysts were prepared using a ferric nitrate solution that was prepared by dissolving  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled and deionized water, and then an amount of orthosilicate needed to make a Si/Fe atomic ratio of 4.6 was added. The mixture was stirred vigorously until the tetraethyl orthosilicate has hydrolyzed. The tetraethyl orthosilicate and iron nitrate mixture was added to a CSTR precipitation vessel where it mixed with a 30% ammonium hydroxide stream. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon molar ratio of 100:4.6 was obtained. The slurry was then filtered with a vacuum drum filter and washed twice with deionized water. The final filter cake was dried for 24 hours in an oven at  $110^\circ\text{C}$  with flowing air. The catalyst was crushed to approximately  $60\ \mu\text{m}$  sized particles and then calcined at  $350^\circ\text{C}$  in an air flow for 4 hours.

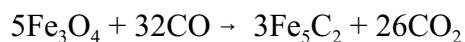
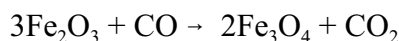
In this study, the 100Fe/4.6Si catalyst base powder was impregnated with the proper amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  to give an atomic composition of 100Fe/4.6Si/2.0Cu. The amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  added will depend on the iron content of the base catalyst following calcination.

In addition to copper, potassium is also an important promoter for an iron catalyst. Although most researchers use the carbonate, it is believed other potassium salts, such as nitrate, hydroxide, fluoride, silicate or permanganate, produce equal results (3). In this study, the iron catalyst was impregnated with an aqueous  $\text{K}_2\text{CO}_3$  solution. The catalyst was dried at  $110^\circ\text{C}$  overnight with good mixing following the impregnation. Thus, catalysts with three different potassium loading of  $\text{K}/\text{Fe} = 0.05, 0.075$  and  $0.10$  were thus prepared for FTS studies.

### In-situ Activation of Catalysts

The iron catalyst needs to be activated with H<sub>2</sub>, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (8,10). It was reported that catalysts activated with CO yielded higher amounts of long-chain hydrocarbons than catalysts activated with syngas or with H<sub>2</sub>. In addition, activation conditions may also influence the performance of the iron catalyst during the course of the run.

In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C and 1.2 MPa for 24 hours. The CO flowed through a catalyst slurry containing 10% solids in 300 mL of Ethylflow (a mixture of decene trimers). The reduction of Fe<sub>2</sub>O<sub>3</sub> with CO occurs in two steps:



In addition, CO<sub>2</sub> may be formed by the Boudouard reaction:



Previous work in our lab showed that approximately 50 % to 75% more carbon was present in the activated catalyst mass than was needed to form Fe<sub>5</sub>C<sub>2</sub> (10). Gradual oxidation of Fe<sub>5</sub>C<sub>2</sub> to Fe<sub>3</sub>O<sub>4</sub> was observed when this iron catalyst was used in FTS.

### Reactor System

A one-liter continuous stirred tank reactor (CSTR) was used in this study (Figure 2). 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 held at 200°C. A warm trap (100°C) and cold trap (0°C) were used to collect light wax and the water plus oil

samples, respectively, by condensing from the vapor phase that was continuously withdrawn from the reactor.

CO and H<sub>2</sub> mass flow controllers were used to provide a simulated synthesis gas of the desired composition. After the catalysts was activated with CO, syngas was introduced at a rate of 3.1 NL/hr/gram-Fe. Reaction conditions were 230°C, 1.2 Mpa, H<sub>2</sub>/CO = 0.67, 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 1 gives a 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. The vapor phase above the slurry passed continuously 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, providing molar compositions of C<sub>1</sub>-C<sub>7</sub> olefins and paraffins as well as for H<sub>2</sub>, CO and CO<sub>2</sub>. 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 formula:

$$\text{Conversion} = 100\% \times (N_{\text{in}} - N_{\text{out}}) \div N_{\text{in}}$$

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 using a HP5890 GC.

## Results and Discussion

### Potassium Effect on Fischer-Tropsch Synthesis Activity

In this study, a CSTR reactor was used under the conditions of 230°C and 175psig (1.20 MPa). Simulated synthesis gas was prepared by mixing CO and H<sub>2</sub> to produce a H<sub>2</sub>:CO ratio of 0.67. Gas feed flow rate was controlled at 3.1 NL/h/g-catalyst. To study the effect of potassium on iron catalyst activities, two series of catalysts were used to produce low and high wax Fischer-Tropsch synthesis products. Low wax or low alpha iron catalysts were prepared to obtain a potassium content less than 2% while high alpha catalysts higher than 5.0%.

The results (Figure 3) show that potassium has a significant effect on FTS catalyst activity when potassium loading was relatively low. Carbon monoxide conversions increased from 14% to 25% as the potassium content increased from K/Fe = 0 to 0.020. However; when potassium was added at levels higher than about K/Fe = 0.050 it did not affect the CO conversion. All three higher potassium-containing catalysts used in this study yielded a stabilized CO conversion of 40%. This shows that the potassium promotion effects for an iron FTS catalyst activity reached a maximum at a K loading of K/Fe = 0.050 or less for synthesis at 230°C.

Figure 4 gives the relation of potassium loading and FTS alpha values. A lower level of K loading significantly increased the alpha value. An increase in K loading from K/Fe = 0.0144 to 0.020 raised the alpha value from 0.71 to 0.85 while a K/Fe of 0.050 loading increased the alpha value to 0.91; however, a further increase in potassium loading did not enhance the alpha value further.

## Induction Period

Three potassium promoted iron catalysts were tested under the same conditions of 1.2 MPa and 230°C. A mixture of known CO and H<sub>2</sub> composition was used as a simulated synthesis gas. Figures 5 and 6 show the CO and H<sub>2</sub> conversion results obtained from these tests. All three catalysts used in this study showed a similar behavior for both hydrogen and carbon monoxide conversions. All catalysts showed an induction period in which the catalysts showed increasing conversion from a low initial point to a peak value before declining to a stable value. The lower potassium loading produced slightly higher maximum conversion and shorter induction period. The peak hydrogen conversion for the K/Fe = 0.050 catalyst was as high as 50% while the K/Fe = 0.10 yielded a 45% peak conversion (Figure 5).

While the induction period and the peak conversion values are slightly dependent of the K loading, the stabilized conversions and the stabilization periods are independent of the potassium content. All three higher potassium promoted catalysts yielded the same stabilized hydrogen conversion at about 400 hours of total on-stream time.

Carbon monoxide conversions showed a behavior that is similar to hydrogen conversions using these K promoted catalysts (Figure 6). K/Fe = 0.0144 catalyst showed an induction period of 25 hours while the K/Fe = 0.05, 0.075 and 0.10 catalysts yielded induction periods of 80, 120 and 150 hours, respectively. After 400 hours of reaction time, CO conversions became stable when high alpha catalysts were used. Figure 6 showed a slight difference in stabilized CO conversions for catalysts with different potassium loadings. The K/Fe = 0.075 catalyst yielded a 50% CO conversion while the K/Fe = 0.05 and 0.10 catalysts produced a CO conversion of 36% and 38%, respectively.

## Selectivity

Table 2 shows the productivity and selectivity of the FTS reactions catalyzed by these high-alpha iron catalysts. Hydrocarbon productivity, CO<sub>2</sub> selectivity and the water gas shift reaction were not significantly influenced by the potassium content at the higher loadings. Only a slight improvement in methane selectivity, water gas shift reaction and hydrogen productivity was observed when potassium content increased from K/Fe of 0.05 to 0.075. A further increase in potassium content did not enhance the productivity and the selectivity of FTS. Gas (C<sub>2</sub>-C<sub>4</sub>) analysis results indicate that the percentage of olefins for each carbon number were in the range of 82 to 87% for all three catalysts (Figures 7-9). Table 2 also indicated that, as potassium content increased from K/Fe of 0.05 to 0.075, long-chain hydrocarbons yield increased significantly from 9.2% to 46.4%. The amount of the gas fraction with increasing potassium content (C<sub>1</sub>-C<sub>4</sub>) decreased by nearly 50% and gasoline (C<sub>5</sub>-C<sub>11</sub>) fraction decreased by over 40%. Further increase of K/Fe from 0.75 to 0.10 did not enhance the production of heavy fractions.

Dry reported that formation of methane is inversely proportional to the concentration of water and carbon dioxide (3), although it was also believed that CO<sub>2</sub> and water favor the formation of methane (13). Figures 10 and 11 show the influence of high loadings of potassium on CO<sub>2</sub> and CH<sub>4</sub> selectivity for low temperature synthesis. Similar to the CO conversion profile, CO<sub>2</sub> selectivity also shows an induction period. The CO<sub>2</sub> selectivity for all three catalysts went through a rapid initial period of increase; however, the induction period for CO<sub>2</sub> is shorter than it is for hydrocarbon formations. The CO<sub>2</sub> selectivity declined from its peak value of 42% to a stable level of 39%. Potassium had little effect on CO<sub>2</sub> selectivity for iron catalysts with K/Fe = 0.05 to 0.10. Figure 11 shows an initial decline in methane selectivity during the first 200 hours of the run. The content of potassium had little effect on the methane selectivity. All three

catalysts yielded a stable methane selectivity of 1.5% after the first 200 hours of run. The results shown in Figures 10 and 11 suggest that the surface structure and/or composition changes in the first 250 hours of the reaction so that it favors the formation of CO<sub>2</sub> and inhibits the formation of methane.

### Reaction Conditions

After both hydrogen and the carbon monoxide conversions were stabilized, FTS reaction temperature was changed from 230 to 250°C using the K/Fe = 0.10 promoted catalyst. As shown in Figure 12, both conversions went through a new induction period and then rapidly reached a stable conversion level. A 20°C temperature increase resulted in a hydrogen conversion change from 36% to a stable level of 50%. Similarly, CO conversion increased from 37% to 57%.

In addition to reaction temperature, total pressure and the H<sub>2</sub>:CO ratio also had an important influence on FTS conversions. A test was conducted using an iron catalyst (K/Fe = 0.075) to study the effect of H<sub>2</sub>:CO ratio on the catalyst activity. Initial reaction conditions were 175psig, 230°C and H<sub>2</sub>:CO ratio of 0.67. After FTS conversions became stable after 500 hours of reaction time, the pressure was increased to 350psig and the H<sub>2</sub>:CO ratio to 1.7. Figure 13 show that a change of the H<sub>2</sub>:CO ratio did not yield stable conversions for H<sub>2</sub> and CO in the initial 200 hours of reaction following the changes in reaction conditions. Immediately after the H<sub>2</sub>:CO ratio was changed, the H<sub>2</sub> conversion decreased significantly from 40% to less than 30%, and then the H<sub>2</sub> conversion declined linearly from 30 to 22% before it approached a stable level. Although carbon monoxide conversion showed an initial increase, it then decreased at a similar rate as the H<sub>2</sub> conversion did.

The results show, as expected, that an increase of the H<sub>2</sub>:CO ratio in the feed gas lowered the H<sub>2</sub> utilization rate. Higher H<sub>2</sub>:CO ratio feedstock gas and/or the higher partial pressures



lowered the FTS catalyst activity, apparently due a slower replenishment of the iron carbide surface than that when a low H<sub>2</sub>:CO ratio gas was used. CO<sub>2</sub> selectivity decreased from 40% to 30% immediately after the gas ratio and pressure were changed, suggesting that water gas shift reaction can be inhibited due to the higher H<sub>2</sub> content in the gas (H<sub>2</sub>:CO = 1.7). The data in Figure 13 also showed a new induction period after the reaction temperature changed from 230 to 270°C. A new stabilized conversion may be expected that is similar to the result given by Figure 12.

## Conclusions

Promoted iron FTS catalysts showed a significant increase in CO conversion up to about K:Fe ratio of 5:100. An increase in (K loading K/Fe = 0.0144 to 0.020) increased the alpha value from 0.71 to 0.85; a further increase to K/Fe = 0.050 increased the alpha value to 0.91.

Catalysts with different potassium loadings showed different lengths of induction, in which the FTS reaction showed increasing conversion from a low initial value to a peak value before declining to a stable activity level. Lower potassium loadings produced a higher maximum conversion and a shorter induction period. Although the induction period and the peak conversion values were dependent of the K loading, the stabilized conversions and the stabilization period were independent of potassium content. All three of the higher level potassium promoted catalysts yielded a stabilized hydrogen conversion at about 400 hours of total on-stream time.

An increase in potassium content to 5:100 = K:Fe substantially enhanced the long-chain hydrocarbon yield with a concurrent decrease in the gas fraction (C<sub>1</sub>-C<sub>4</sub>) by nearly 50% and the gasoline(C<sub>5</sub>-C<sub>11</sub>) fraction by over 40%. Further increase in potassium iron ratio from K/Fe = 0.075 to 0.10 did not further enhance the production of the heavy fraction. Similar to the CO

conversion profile, CO<sub>2</sub> selectivity also shows an induction period. The CO<sub>2</sub> selectivity for all three catalysts went through a rapid increase during the initial period and then declined from its peak value of 42% to a stable level of 39%. Potassium had little effect on CO<sub>2</sub> selectivity for K/Fe ratios in the range of 5:100 to 10:100 for the potassium promoted catalysts. Methane selectivity declined gradually during the first 250 hours of run. All three higher potassium-containing catalysts yielded a stable methane selectivity of 1.5% after the first 250 hours of run. The surface structure and/or composition changes in the first 250 hours of reaction favor the formation of CO<sub>2</sub> but inhibit the formation of methane. All three potassium promoted catalysts yielded a stable CO<sub>2</sub> selectivity of 38-39% and methane 1.5%.

Increase in reaction temperature resulted in a new induction period and a new higher activity than before the reaction temperature was increased. In addition to reaction temperature and pressure, H<sub>2</sub>:CO ratio also had an important influence on FTS conversions. Increase of the H<sub>2</sub>:CO ratio in the feedstock gas lowered the H<sub>2</sub> utilization rate. Higher H<sub>2</sub>:CO ratio feedstock gas lowered the FTS catalyst activity due to the lower iron carbide formation rate than that when a low H<sub>2</sub>:CO ratio gas was used. CO<sub>2</sub> selectivity decreased immediately after the H<sub>2</sub>:CO ratio increased, suggesting that water gas shift reaction be inhibited due to the higher H<sub>2</sub> content in the gas of H<sub>2</sub>:CO ratio of 1.7.

### **Acknowledgment**

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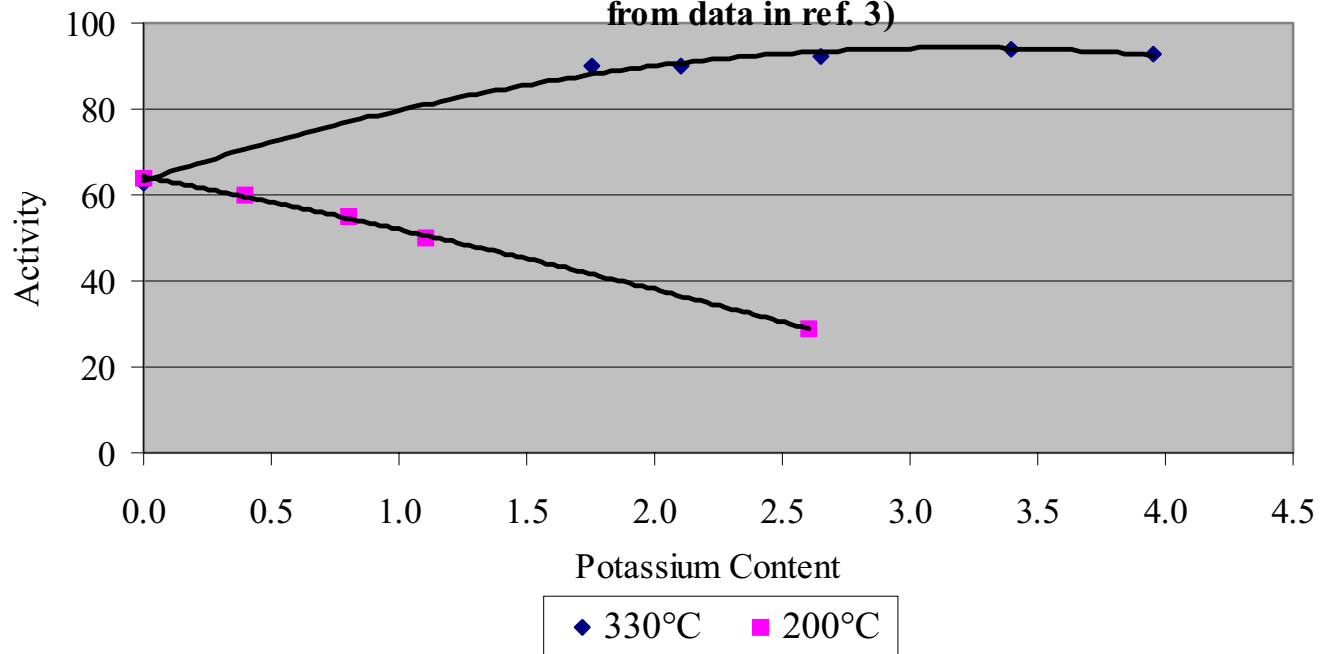
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Table 1		
Analyzers for FTS Products		
Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5890 GC	Water	FID
HP 5790A GC	Oil + Light Wax	TCD
HP 5890 Series II Plus	Heavy Wax	FID

Table 2			
Productivity and Selectivity for Potassium Promoted Catalysts			
Catalyst	5.0%	7.5%	10.0%
Conversion			
CO	38	41	39
H <sub>2</sub>	40	40	39
Syngas	39	40	39
Productivity			
Hydrocarbon, g/hr/g-Catalyst	0.28	0.29	0.28
Hydrocarbon, g/h/Nm <sup>3</sup> -Syngas	145	153	148
Methane, mol/h	0.279	0.329	0.318
Ethene, mol/h	0.181	0.213	0.210
Ethane, mol/h	0.032	0.040	0.040
Propene, mol/h	0.196	0.023	0.225
Propane, mol/h	0.029	0.003	0.035
Butene, mol/h	0.113	0.144	0.124
Butane, mol/h	0.022	0.053	0.027
Water-Gas Shift			
K <sub>p</sub> <sup>a</sup>	2.0	2.3	2.1
H <sub>2</sub> :CO usage <sup>b</sup>			
Selectivity			
CO <sub>2</sub> , mol% <sup>c</sup>	38	40	39
CH <sub>4</sub> , mol% <sup>d</sup>	1.43	1.44	1.61
Olefin ratio <sup>e</sup>			
C <sub>2</sub>	85	85	84
C <sub>3</sub>	87	87	87
C <sub>4</sub>	84	87	82
<p><i>a.</i> <math>K_p = [P_{H_2} P_{CO_2}] / [P_{CO} P_{H_2O}]</math></p> <p><i>b.</i> <math>Usage = r_{H_2} / r_{CO}</math></p> <p><i>c.</i> CO<sub>2</sub> mole% = CO<sub>2</sub> formed/CO converted.</p> <p><i>d.</i> CH<sub>4</sub> mole% = CH<sub>4</sub>/all hydrocarbons.</p> <p><i>e.</i> Olefin ratio = olefin/[olefin + paraffin].</p>			

Figure 1. Potassium effect on relative activity (drawn from data in ref. 3)



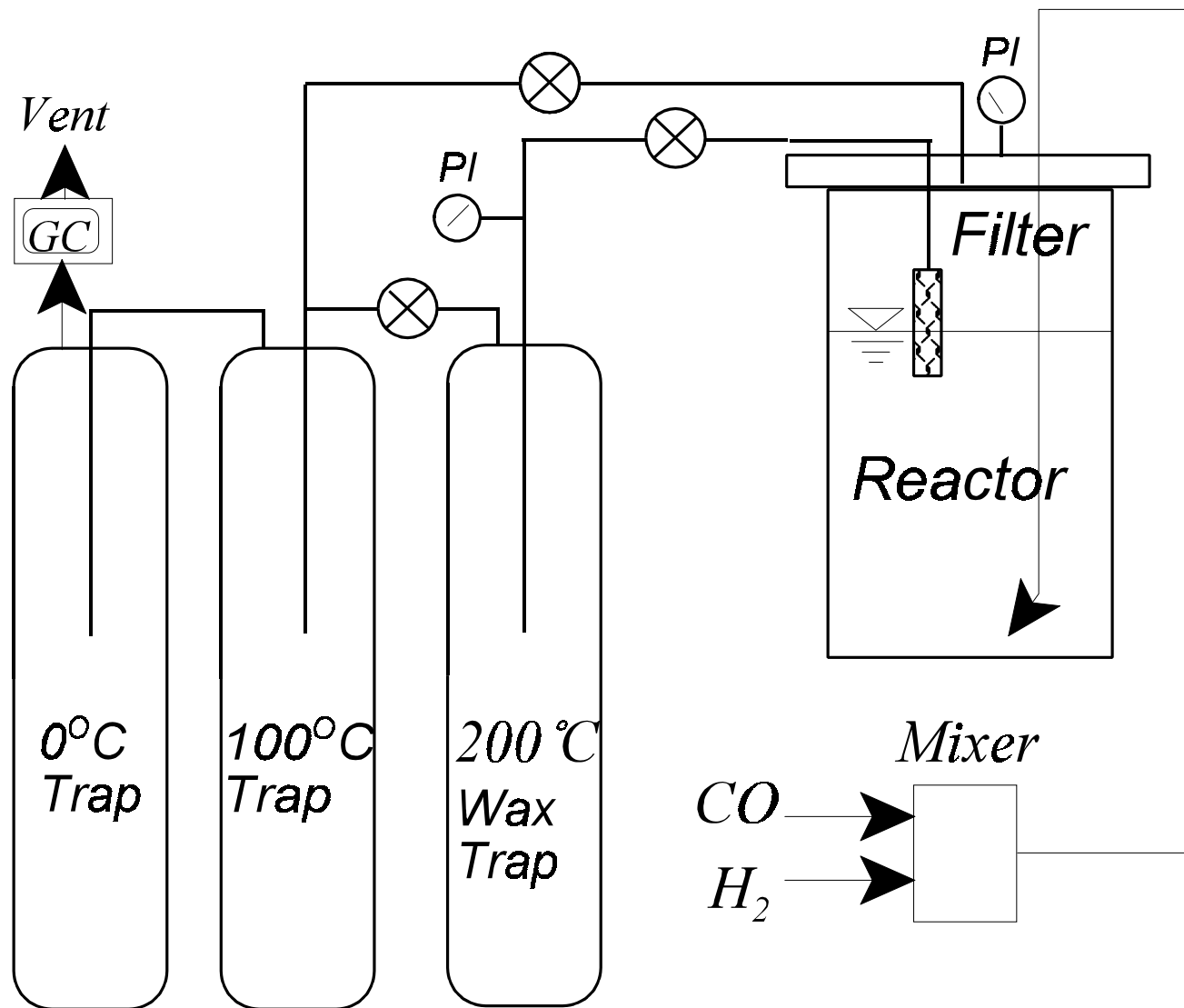
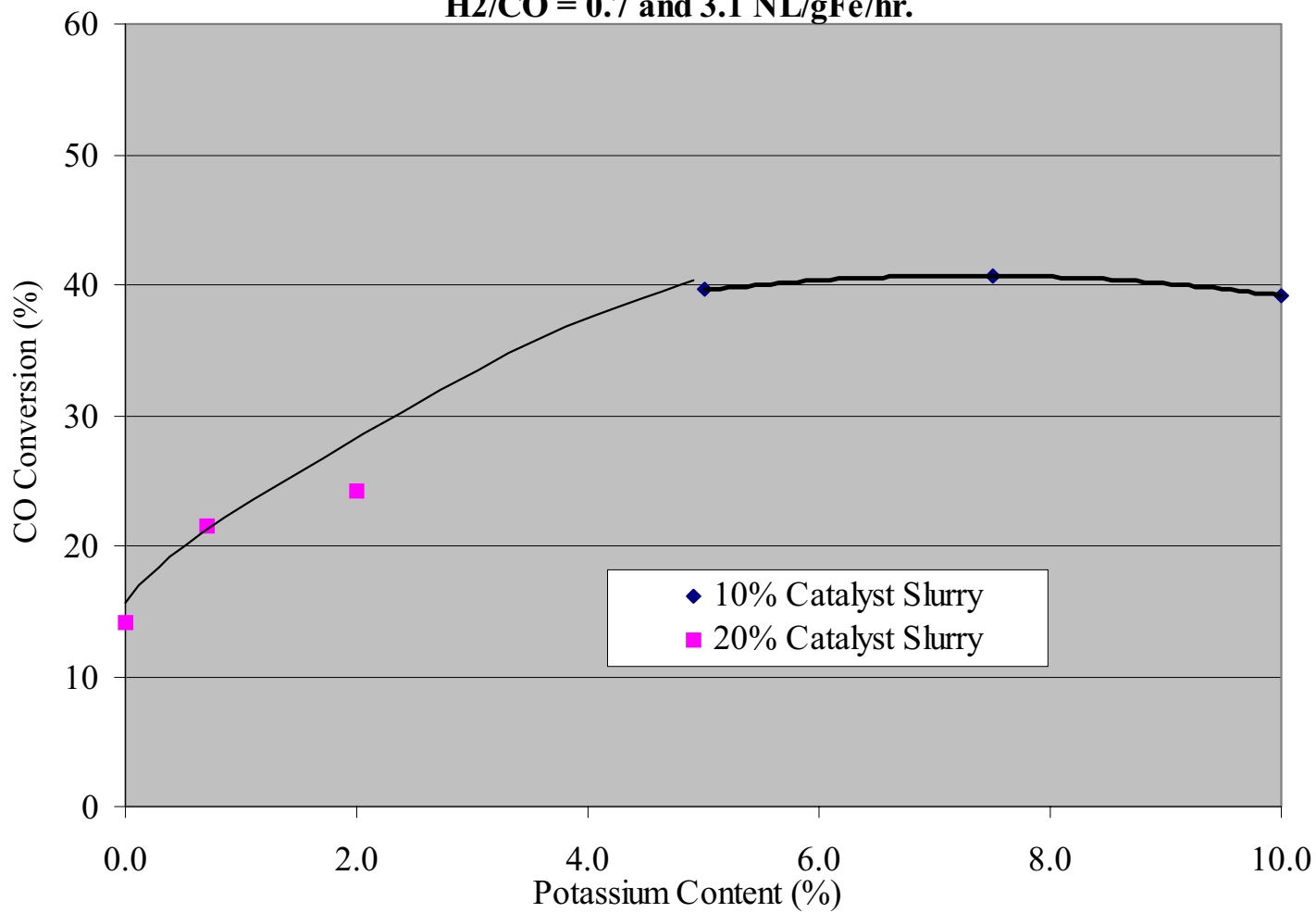


Figure 2. CSTR FTS Reactor System

**Figure 3. Potassium effect on Fe catalyst activity at 230oC, 175 psig,  
H<sub>2</sub>/CO = 0.7 and 3.1 NL/gFe/hr.**





**Figure 4. Potassium Effect on Alpha Values**

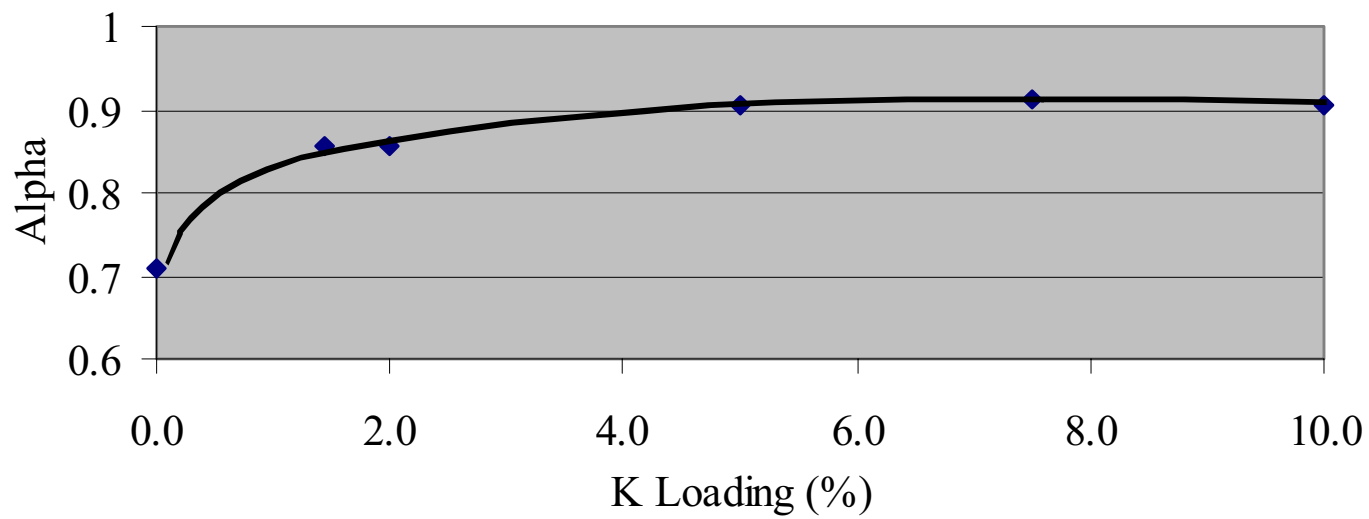


Figure 5. Potassium Effect on H<sub>2</sub> Conversion

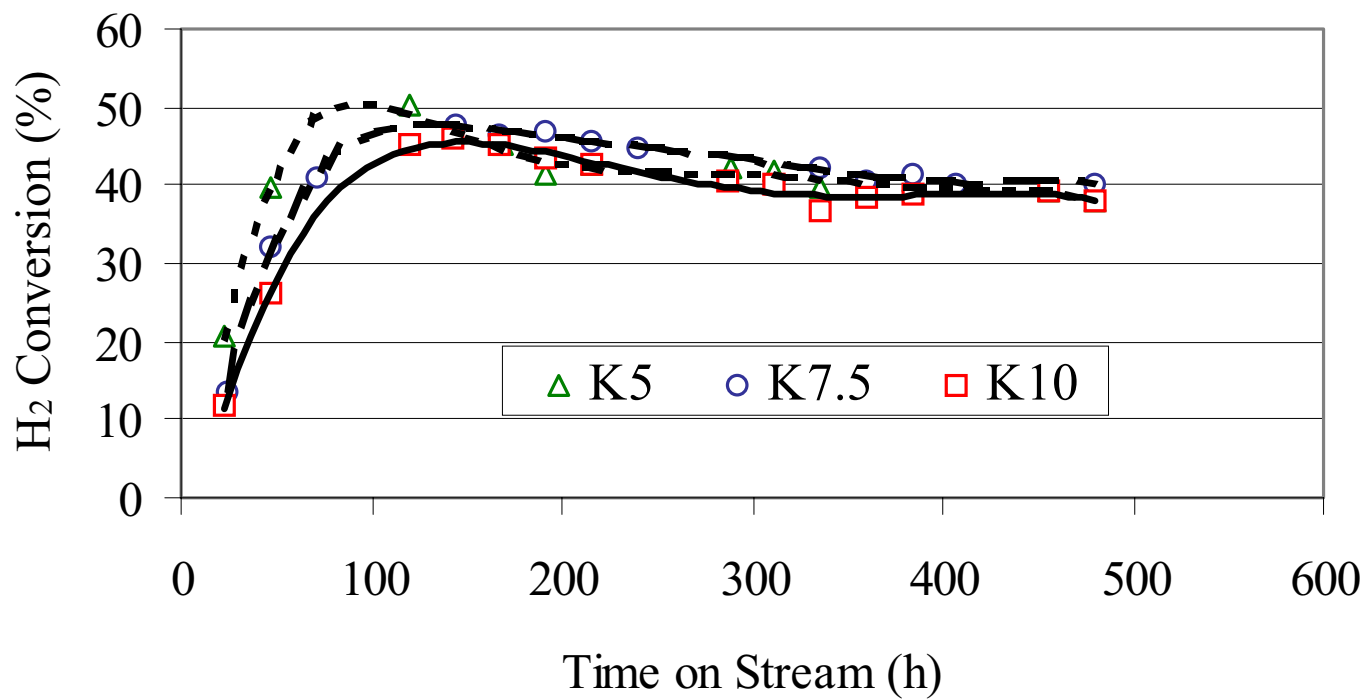


Figure 6. Potassium Effect on CO Conversion

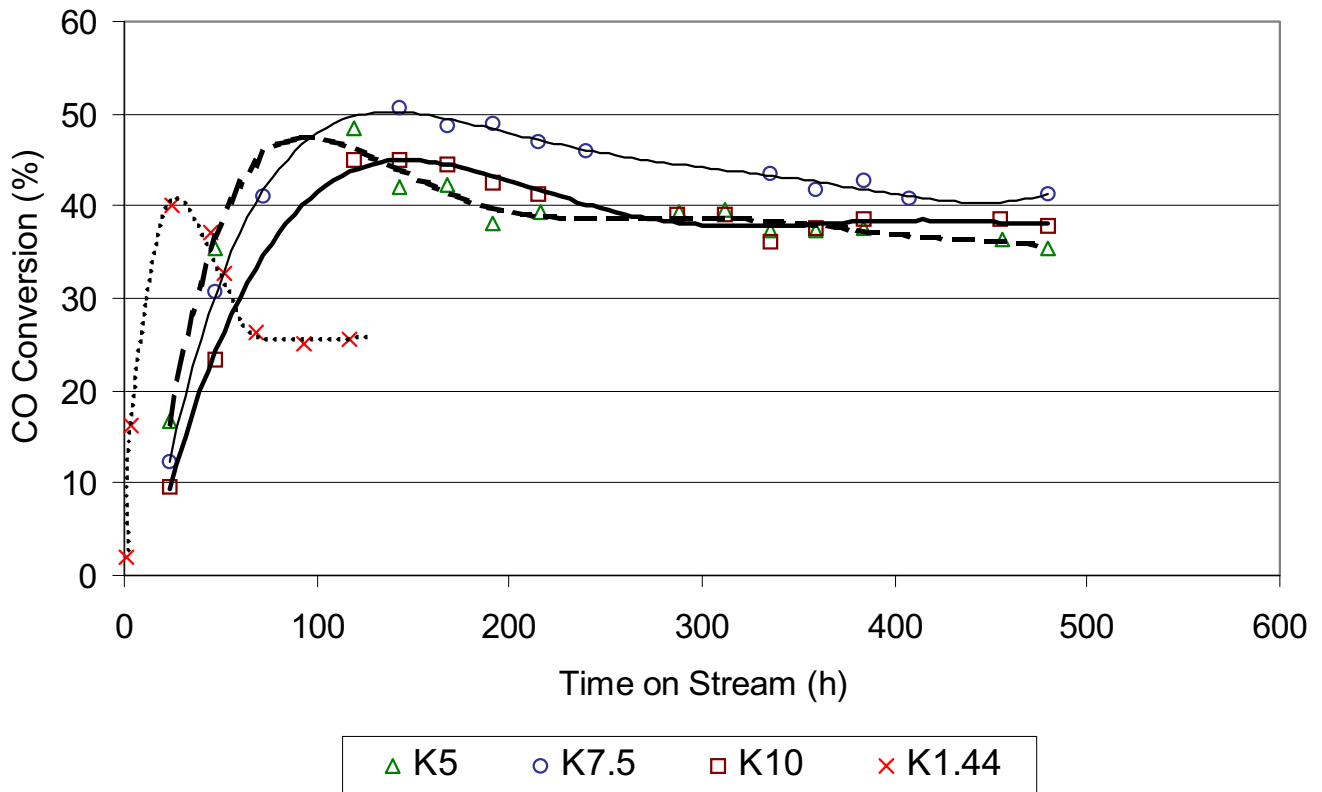


Figure 7. Olefin Ratio (C<sub>2</sub>)

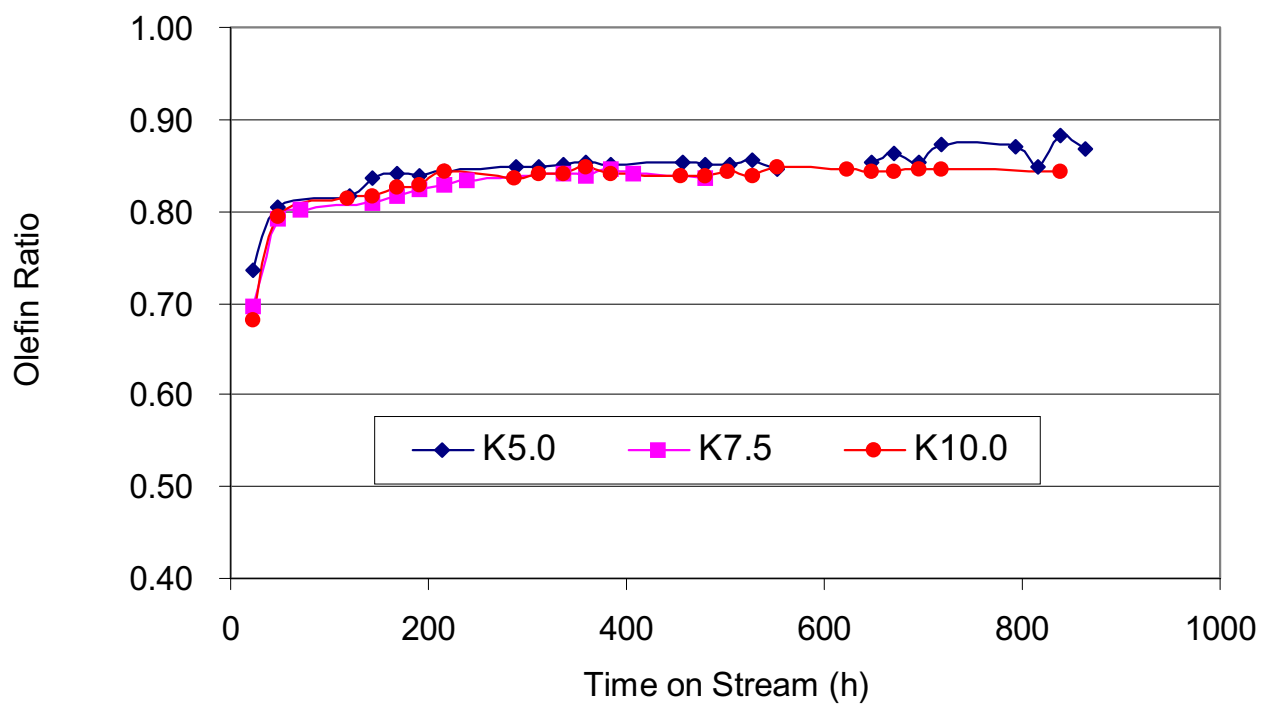


Figure 8. Olefin to Parafin Ratio (C<sub>3</sub>)

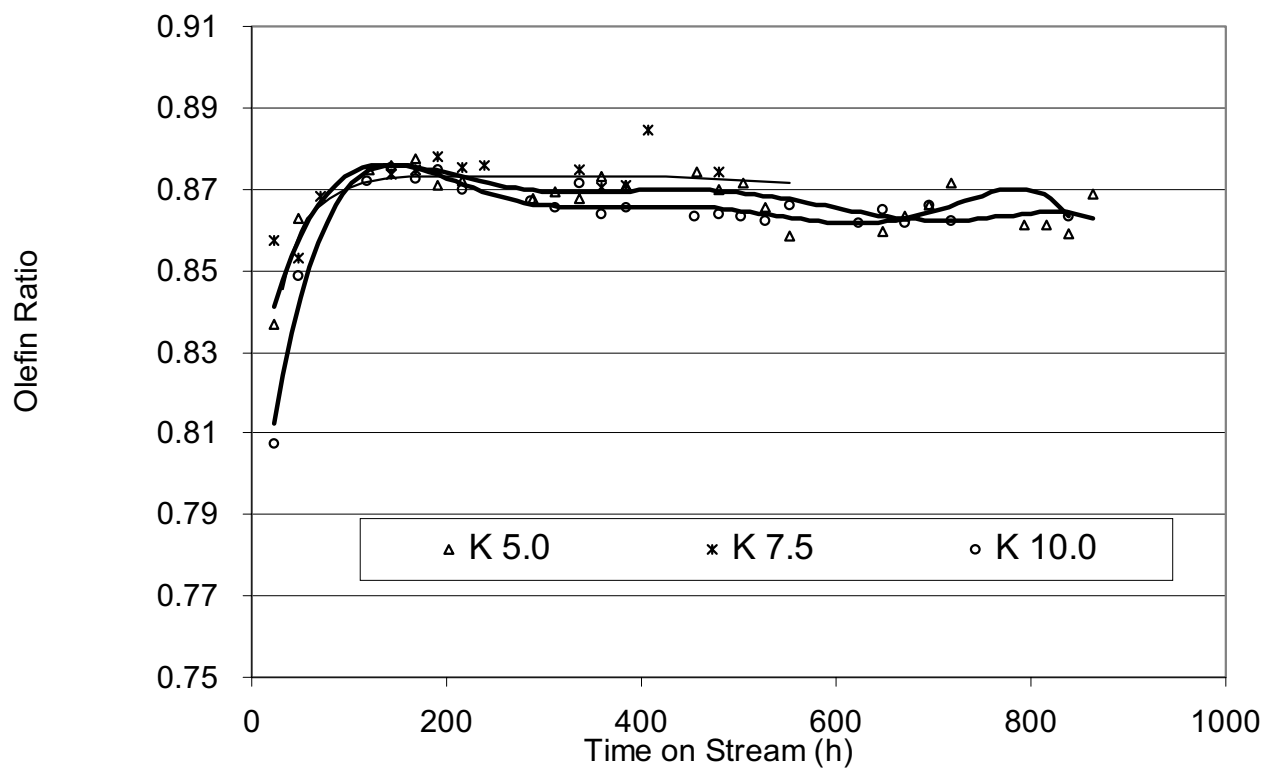
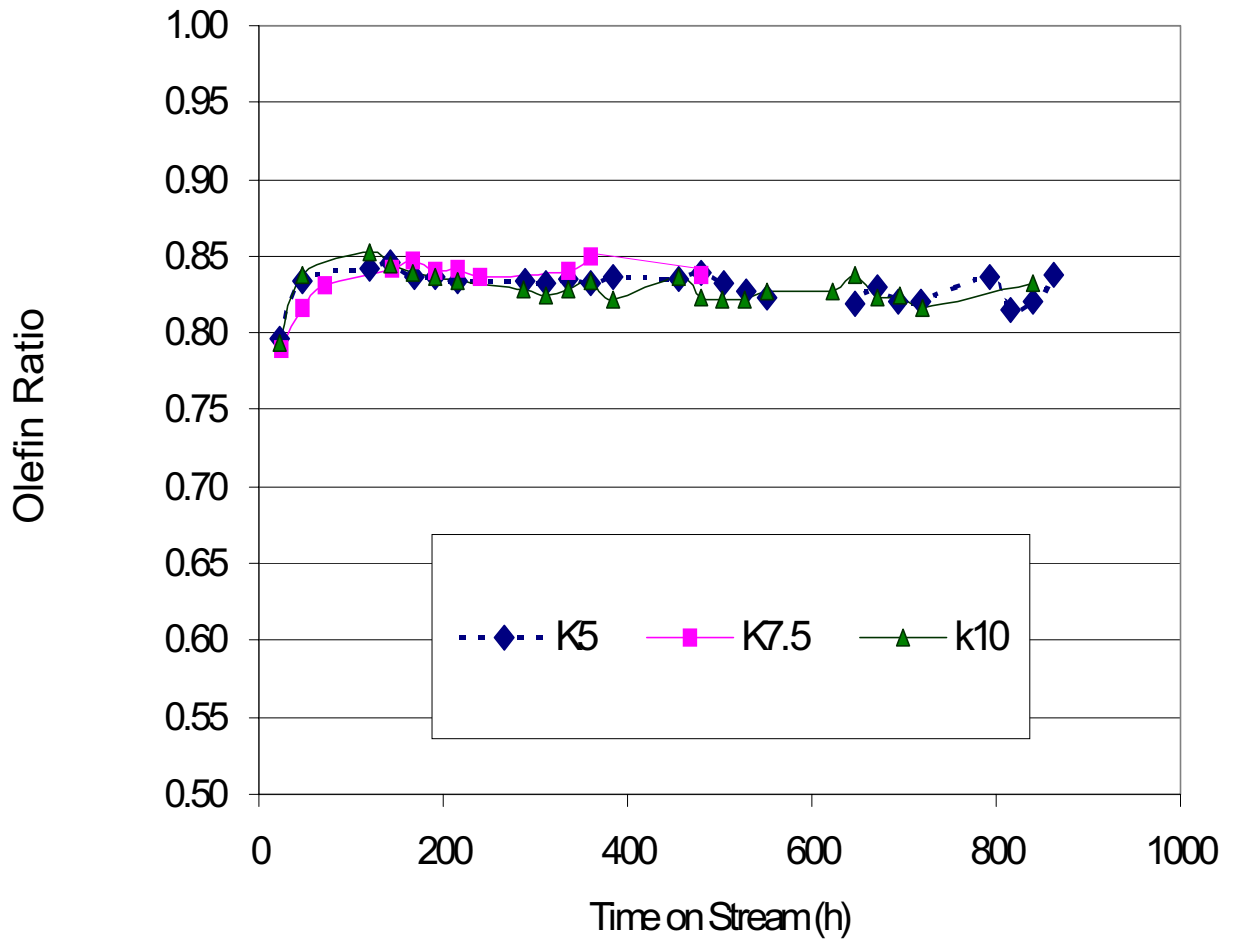


Figure 9. Olefin Ratio ( $C_4$ )



**Figure 10. Potassium Effect on CO<sub>2</sub> Selectivity**

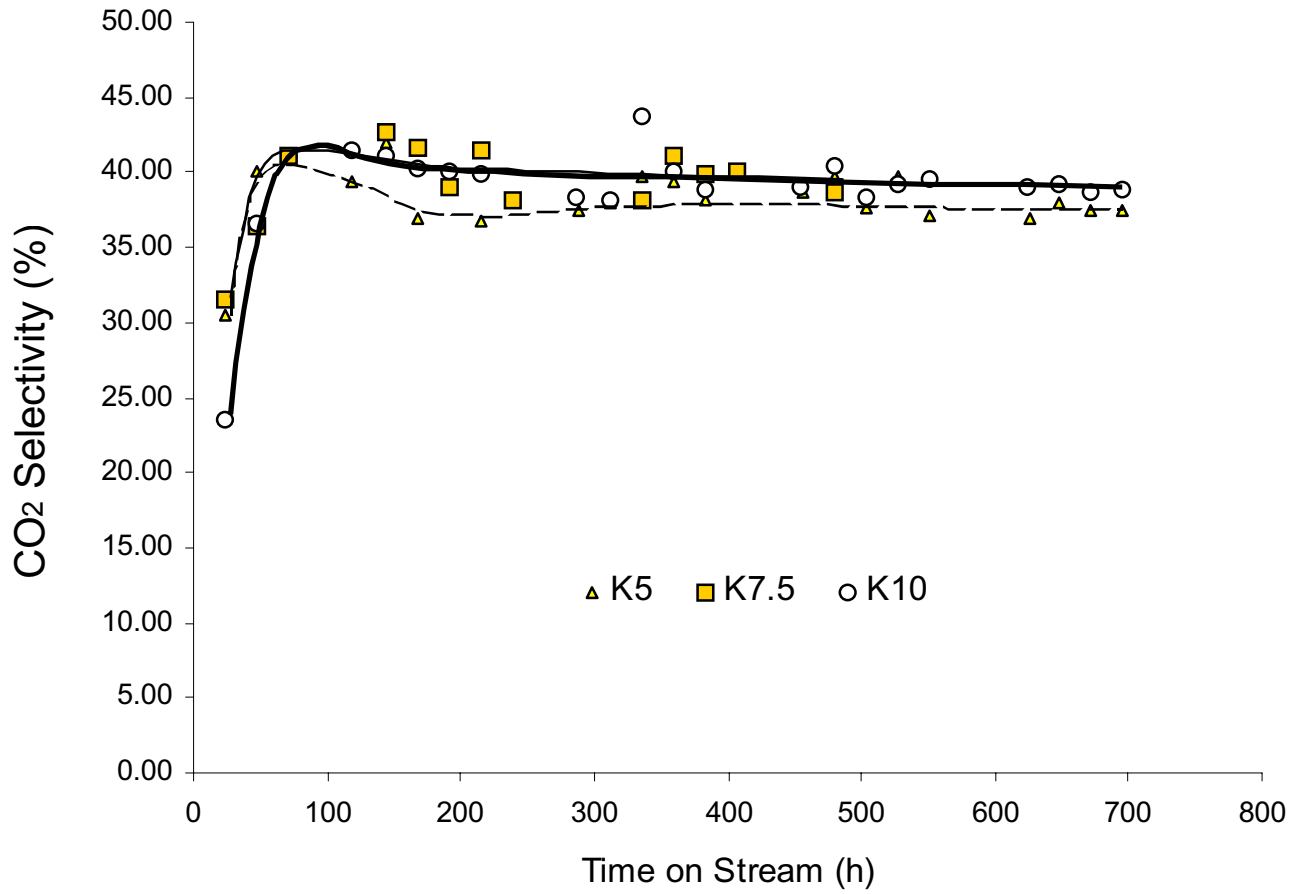


Figure 11. Potassium Effect on CH<sub>4</sub> Selectivity

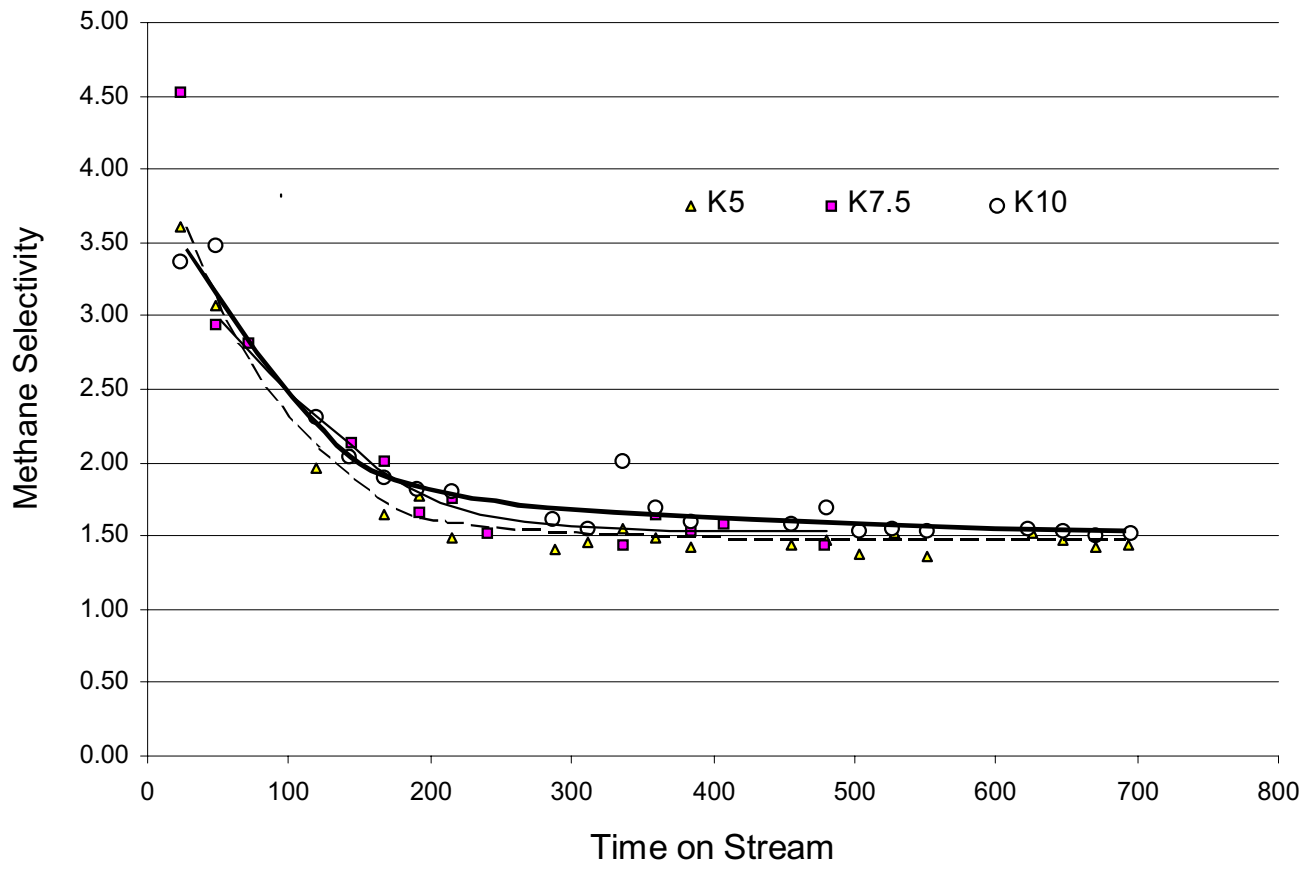




Figure 12. Effect of Temperature on FTS Conversions

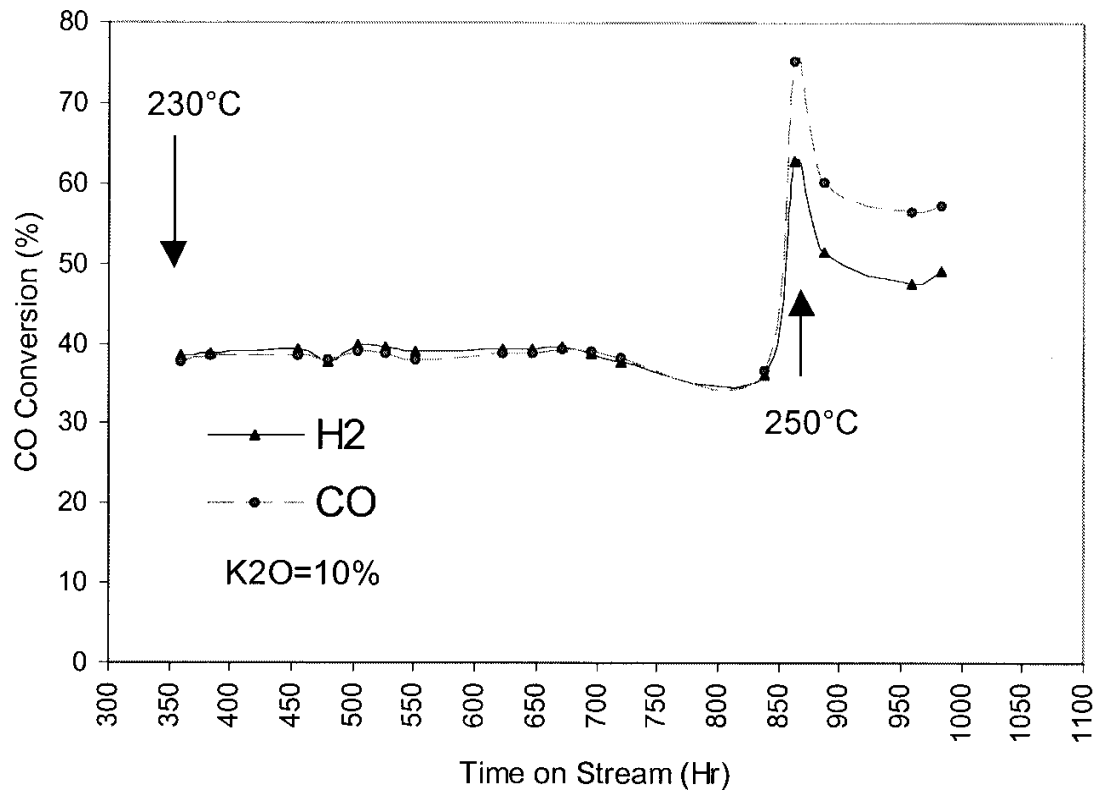


Figure 13. Effect of gas composition and temperature on FTS conversions.

