3.0 RESULTS AND DISCUSSION

3.1 Development of Improved Supported Catalyst Compositions

3.1.1 Basecase Catalyst Preparation and Reproducibility

Basecase catalyst ($Co/Zr/Al_2O_3$), as well as most all other catalysts, was prepared by impregnation (to incipient wetness) of the supports with separate solutions containing the promoter and metal source. All of the catalysts prepared during this contract are listed in Table 1. They were all prepared using metal carbonyls unless otherwise noted. The first goal was to improve the reproducibility of the catalyst preparation over what had been obtained in the prior contract. This was addressed by preparing several $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ compositions using the same procedure but varying the absolute amounts while keeping the metal precursor to support mass ratios constant. The reproducibility was demonstrated by examining the constant Co to Zr ratio that was obtained, which had a mean value of 0.558 and a standard deviation of only 0.0075. The cobalt and zirconium loadings and Co to Zr ratios for the four batches were as follows:

Catalyst Batch #	Amount Prepared, grams	Wt% Co	Wt% Zr	Co/Zr
7864-618-191	55	3.65	6.65	0.55
7864-720-261	30	3.55	6.19	0.57
7864-82-291	30	3.75	6.90	0.55
7864-1010-371	275	3.81	6.84	0.56

As shown in the table, the fourth batch was a large scale preparation that still showed good reproducibility. This batch was prepared to have enough for both gas-phase testing and duplicate slurry-phase runs in the one-liter autoclave. This batch was also considered the baseline composition. The scaled-up preparation procedure was used for all catalysts tested in the slurry reactor.

3.1.2 Basecase Catalyst Performance

The basecase catalyst composition of $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ (batch #7864-1010-371) was tested in both the gas-phase and slurry reactors to establish baseline performance. The metal loadings on this catalyst were 3.8% Co and 6.8% Zr giving a Co/Zr weight ratio of 0.56.

These baseline tests utilized a gas-phase activation procedure (developed under the previous contract) which involved heating the catalyst to 180°C under a N_2 purge at atmospheric pressure, then switching to 1:1 CO/H_2 while heating to reaction temperature and finally increasing the pressure to the desired level. This is mentioned to emphasize that the baseline results for these runs will reflect the type of activation procedure. Later in the project a change was made in the activation procedure based on studies of its effect on performance.

Gas-phase results for this basecase $Co/Zr/Al_2O_3$ catalyst (see Table 1, run #7977-28-371) were analogous to the results obtained in the previous contract for this composition. At test conditions of 240°C, 300 psig, CO/H_2 = 1.0 and GHSV = 986 hr^{-1}, the total syngas conversion was 56% with bulk activity = 27 mols syngas/kg cat/hr and specific activity = 0.26 mols CO/mol Co/min. A slight enhancement in the production of fuel range hydrocarbons was observed, but overall reproducibility of the previous contract results was good.

The baseline slurry-phase test (run #7595-60-C48.4) was carried out for 1330 hours in order to establish a basis for comparison to the previous contract results and to other catalysts developed in the current contract. Another objective was to determine the extent, if any, of mass transfer effects in our slurry reactor at standard operating conditions. A summary of the basecase slurry test results is presented in Table 3 and in Figures 1 and 2.

Initially at 220°C, CO/H_2 = 1.0, 300 psig, 1.65 h^{-1} SV, and 1200 rpm, both activity and product selectivity were very stable. The bulk activity was 13.0 mols syngas/kg cat/hr with no appreciable deviation in hydrocarbon distribution from the standard Schulz-Flory distribution, as shown in Figure 3. This is comparable to the 7-14 mols syngas/kg cat/hr bulk activity range obtained in the previous contract. After the change to 250°C and CO/H_2 to 1.5, problems in maintaining a constant slurry level developed as a result of the high catalyst activity. Even with regular tapping of the reactor, the wax product accumulated in the partial reflux condenser and eventually was forced into the exit line causing plugging of the back pressure regulator. At 349 hours the reactor was placed under a N_2 purge and the temperature lowered to 180°C for 102 hours to clean up the exit lines, replace the back pressure regulator and remove excess product. To avoid such problems in the future, a thermocouple was placed within the partial reflux condenser. Monitoring gross temperature changes in the condenser due to product accumulation and/or catalyst migration provided an additional check on slurry volume.

To establish baseline data at 250°C, $CO/H_2 = 1.5$, $SV = 1.64$, 500 psig and 1200 rpm, the reactor was run for an additional 220 hours. During this time, the activity and selectivity returned to a stable level once more. The average bulk activity improved to 19.0 mols syngas/kg cat/hr. These conditions favored heavier molecular weight product formation but with no substantial deviation in the Schulz-Flory distribution, as shown in Figure 4. Again, the activity at these conditions was similar to that obtained in the previous contract.

After establishing baseline performance at 220° and 250°C, mass transfer effects were determined by running at different stirrer speeds. The results, tabulated in Table 4, are average values over the duration of tests at the stated conditions. At 250°C with the stirrer speed at 1200 rpm, the bulk activity was 19.0 mols syngas/kg cat/hr. When the stirrer speed was increased to 1600 rpm there was only a small change in bulk activity to 17.2 mols syngas/kg cat/hr, which was actually in the opposite direction of what would be expected had there been mass transfer limitations. Likewise at 280°C there was no effect of stirrer speed on bulk activity. Hydrocarbon selectivity also showed no dependence on stirrer speed at either temperature. These results indicated that mass transfer from the gas/liquid interface to the bulk liquid, as well as transfer through the liquid to the solid, was negligible in our reactor at normal operating conditions.

Finally baseline performance at 280°C was established with a CO/H_2 feed ratio of 1.57, SV = 1.64 and 300 psig. Bulk activity stabilized at 24 mols syngas/kg cat/hr with total syngas conversion at 33%. Methane selectivity increased dramatically from 14 wt% at 250°C to 26 wt% at 280°C (see Figure 5).

3.1.3 Conventional Catalyst Preparation and Performance

Since a major objective of our research was to study the use of metal carbonyls as catalyst precursors, a comparison to conventionally prepared catalysts was necessary. This was done by examining catalysts prepared from cobalt nitrate using the same support and promoter as the cobalt carbonyl-based catalysts. The activity and selectivity of the two catalysts (batches 8466-4 and 8466-2) in the slurry-phase reactor (runs 8523-1-4 and 7888-85-2) are compared in Table 5. Hydrogen activation was used in both runs.

Both catalysts had similar cobalt and promoter loadings. Performance differences were larger at lower temperatures. At 240°C, bulk activity of the carbonyl catalyst was more than twice that of the nitrate catalyst, while specific activity was three times higher. At 260°C, the carbonyl catalyst still outperformed the nitrate catalyst in both bulk activity (29% increase) and specific activity (52% increase). The carbonyl-prepared catalyst also provided better liquid fuel selectivity at both temperatures, producing less methane but more light hydrocarbons (C_{2-4}). The major difference was in the production of heavier hydrocarbons, with the nitrate-derived catalyst giving significantly higher C_{24+} selectivity. These differences are likely related to metal particle sizes, although specific data needs to be determined.

The performance of the cobalt carbonyl-based catalyst was also compared with that of a cobalt nitrate-based catalyst patented by Shell (6). The Shell patent states an optimum Co loading of 17-19%. The cobalt carbonyl-based catalyst was thus prepared with a similar loading (as reduced Co metal). Comparisons were from gas phase tests only. A major difference in hydrocarbon selectivity was also observed, with the Shell catalyst producing greater amounts of heavy products. The hydrocarbon product distributions are compared in Figure 6.

3.1.4 Catalyst Activation Studies

The type of activation used for "conventional" FT catalysts has been shown by several researchers to affect performance(7). Dry(8) detailed the effects of activation on the performance of precipitated and fused iron catalysts and indicated that pure H_2 was preferred. Another recent study of catalyst performance vs. degree of reduction for $Co(NO_3)_2$ on alumina used only H_2 reduction(9). The activation of supported metal carbonyl catalysts has generally been done by thermal decomposition under vacuum or inert atmosphere(10). Carbonyl groups are lost to give the active metal. Although the effect of reducing gases such as H_2 and syngas on supported metal carbonyls has not been well established, these gases should improve the degree of metal reduction since the metals are initially oxidized by the support.

The present study of activation conditions compared pure H_2 activation with syngas ($CO/H_2 = 1$) activation using the 4% Co on zirconium-promoted alumina catalyst (batch 8466-4 vs. 7864-1010-371). Hydrogen activation significantly improved both activity and liquid fuel selectivity in the slurry tests. Figure 7 compares syngas conversion following both types of activation as a function of temperature and space velocity. At comparable reaction conditions, H_2 activation converted 30 to 40% more syngas in the 220 to 260°C range, but at 280°C the difference was less. For H_2-activated catalyst at lower space velocity the syngas conversion appeared to be independent of temperature between 240 and 280°C.

Table 6 shows that H_2 activation increased the C_{5-23} selectivity by 25 relative percent, from 57 to 71 wt%, and decreased both the CH_4 and wax selectivity. The selectivity still corresponded to the Schulz-Flory distribution. The increased activity probably resulted from a higher degree of Co reduction, but the reason for the enhanced liquid fuel selectivity is less clear. Perhaps the degree of reduction and metal particle sizes, which both depend on activation conditions, together affect chain growth probability. However, catalysts from different activation procedures were not examined for these two properties.

3.1.5 Promoter Studies

As with Fe catalysts, promoters were found to enhance the selectivity and stability of Co catalysts during the FT catalyst development era in Germany. However there appears to be less understanding of how the promoters function in Co catalysts than in Fe catalysts. Development of the precipitated Co catalysts in Germany led to the use of ThO_2 as a promoter to enharce the average molecular weight of the hydrocarbon product. MgO was also added as a structural promoter which lowered the deactivation rate of the catalyst. More recently, Russian workers showed that the use of ZrO_2/MgO or TiO_2/MgO in place of ThO_2/MgO gave equally high liquid yields. Previous work at Air Products showed that ZrO_2 on Al_2O_3 also gave enhanced liquid yields.

In the current study, the effectiveness of zirconium as a promoter was compared to that of titanium for both the Co/Al_2O_3 and Co/SiO_2 catalysts. Catalysts were prepared using analogous procedures with the source of promoter being the alkoxides. Cobalt to promoter atomic ratios were held constant.

Gas phase test results are compared in Table 7. The titanium promoted catalysts for both the alumina and silica supports showed lower activity than with zirconium. For the Co/Al_2O_3 catalyst this decrease in bulk activity was 20% at 240°C. The titanium promoted Co/SiO_2 catalyst had 40% lower bulk activity than the zirconium promoted catalyst at 240°C.

The hydrocarbon selectivity was also different for the two promoters as shown in Table 8. There was an increase in methane and light hydrocarbon selectivity with the titanium promoter, with the C_{5-11} fraction predominating. The liquid fuel selectivity was in the 52-62% range with the titanium promoter. This compares to 72% C_{5-23} selectivity with the zirconium promoter. Titanium did enhance the light olefin (C_{3-5}) selectivity as shown by the olefin/alkane ratios in Table 9. The hydrocarbon selectivity to C_{3-5} olefins was particularly high at the lower temperatures.

The lower activity found with titanium in the gas phase tests was also observed in the slurry phase reactor as shown in Table 10 for the Co/SiO_2 catalyst. With titanium the bulk activity was 50% lower at 240°C and 33% lower at 260°C. Differences in hydrocarbon selectivity were less apparent in the slurry phase.

Other than testing Co/Al_2O_3 and Co/SiO_2 catalysts without any promoter, no other promoters were examined. Results for unpromoted catalyst are discussed in Section 3.1.7.

3.1.6 Support Studies

The type of support also had a major influence on catalyst activity, as shown in Figure 8. These studies were done in the fixed-bed reactor, although the Al_2O_3-, SiO_2- and $MgO{\bullet}3.6SiO_2$-supported catalysts were also studied in the slurry reactor. The slurry reactor data is found in Table 2. These catalysts all had similar cobalt and promoter loadings, except for the TiO_2-supported catalyst, which had no promoter. The silica-supported catalyst was approximately twice as active as all the others. This may be due to the low reactivity between cobalt carbonyl and silica as opposed to the high reactivity of the other supports towards metal carbonyls(13).

A surface area effect had to be determined also, since the silica catalyst had 50% greater surface area than the alumina catalyst. To examine this effect a Co/Zr/silica catalyst having the same surface area as the Co/Zr/alumina catalyst was tested. The bulk and specific activities of the silica catalyst were 50-60% greater than those of the alumina catalyst at similar conditions as shown in Figure 9. The high surface silica catalyst, however, was still the most active with 30-50% greater bulk activity than the low surface silica catalyst. Thus silica does provide an inherently more active catalyst than alumina but some of the enhancement that was initially observed was due to the increased surface area. The hydrocarbon selectivity was similar for both high and low surface area Co/Zr/silica catalysts.

A more detailed comparison of the properties of the alumina and silica supports was performed. The properties are listed in Table II. Comparison of the porosity of the low surface area silica with that of the alumina and high surface silica indicated that there was no relationship between the macropore or micropore volumes and catalyst activity. The micropore volume of the alumina was between that of the silica supports, which were the two best. Catalyst activity did increase as the total pore volume of the support increased. There was no relationship between average pore diameter and catalyst activity.

3.1.7 Metal to Promoter Ratio

To study the effect of Co-to-promoter ratio on the performance of the silica-supported catalysts, the following four Co/Zr/silica catalysts were prepared:

Catalyst #	Wt% Co	Wt% Zr	Co/Zr
8466-45	4.0	4.8	0.83
8466-46	4.4	2.3	1.9
8466-47	4.6	0.7	6.6
8466-49	4.2	0	∞

The cobalt loading was kept close to 4 wt%, while the zirconium loading was progressively lowered. This gave a series of catalysts, including the basecase catalyst, having Co-to-Zr ratios of 0.53, 0.83, 1.9, 6.6 and a final catalyst having no added promoter.

The effect of Co/Zr ratio on gas-phase bulk and specific activities for this series of silica-supported catalysts is plotted in Figures 10 and 11. For optimum bulk activity it appears that the Co/Zr ratio should be closer to 1 than to the basecase value of 0.5. Specific activity, however, was best for the basecase catalyst. The usage ratio followed a trend toward higher values as the zirconium content increased. Total fuels selectivity was also best for the basecase catalyst, especially if straight run liquid fuels (C_{5-18}) was desired. Overall, it then appears that the optimum Co/Zr ratio is near 0.5, although lower ratios were not investigated.

The effect of cobalt to zirconium ratio on the slurry-phase activity of the Co/Zr/silica catalysts is shown in Figure 12. Of the 5 catalysts tested in the gas-phase, 3 of them were compared in slurry-phase tests. The 3 catalysts had Co-to-Zr ratios of 0.53 (basecase, catalyst #8466-18), 1.9 (catalyst #8466-46) and a final catalyst with no promoter (catalyst #8466-49). The trend of decreasing activity with decreasing amounts of promoter was analogous to what was observed in the gas phase. The trend was more pronounced at higher space velocity. Thus, as in the gas-phase, the optimum Co-to-promoter ratio was 0.5.

3.1.8 Metal Loading

The effect of increasing metal loadings on the performance of the Co/Zr/silica catalyst was examined with gas phase tests of 11.0% (batch #8466-58) and 14.4% (batch #8466-63) Co catalysts, as well as the basecase 3.5% Co catalyst. There were several reasons for not keeping the Co-to-Zr ratio at 0.53, which was the ratio used in the basecase catalyst. One reason was based on the results of examining the effect of Co/Zr ratio on performance, which showed that the best bulk activity was achieved when the Co/Zr ratio was between 1.0 and 2.0. A second reason was based on a desire to prepare a Co/Zr/silica catalyst having a composition analogous to that used by Shell Oil Co. in their Middle Distillate Process™. This would enable us to make a direct comparison between the two different preparation methods. Comparing bulk activity trends as the metal loading was increased (Figure 13) reveals that relatively small changes occurred on increasing from 3.5 to 11.0% Co at 220° and 240°C, while increasing to 14.4% Co resulted in a large decline in bulk activity at all temperatures. The 11.0% Co catalyst gave the highest syngas conversion (52%) at 220°C of any catalyst tested at this temperature during this contract. Perhaps the 11.0% Co catalyst can be optimized to give the highest bulk activity at all temperatures.

Bulk catalyst density also increased as the metal loading was increased as follows:

Catalyst #	Wt% Co	Bulk Density
8466-18	3.5	0.394 g/cc
8466-58	11.0	0.564
8466-63	14.4	0.883

Since the catalyst bed volume was 10-cc for each test the actual weight of cobalt in the reactor increased by a larger factor than the increase in weight percent metal loadings and the space velocity based on the weight of cobalt decreased. These gas phase tests were done at similar feed gas flow rates and thus bulk activity may have been more affected by changes in bulk density. Quantification of this would be difficult without running the tests at a constant weight hourly space velocity.

Selectivity to liquid fuel product (C_{5-23}) declined with increasing Co loading with a general flattening of the hydrocarbon distribution. Overall the catalyst having the lowest Co loading was the best in terms of activity and selectivity.

Two Co/Zr/silica catalysts having different Co loadings were compared in the slurry-phase reactor (Figure 11). Unlike the gas-phase results, at both 240° and 260°C the bulk activity declined as the Co loading increased from 3.5 to 11.0%. Selectivity to liquid fuel product (C_{5-23}) decreased slightly when the CO/H_2 feed ratio was 1.0 but increased when $CO/H_2 = 0.5$.

3.1.9 Other Metals

A $Ru/Zr/Al_2O_3$ catalyst prepared from $Ru_3(CO)_{12}$ was found to be a promising catalyst during the previous contract program. A large scale batch (150 g) of this catalyst was prepared using the new reproducible procedure developed for the $Co/Zr/Al_2O_3$ catalyst.

Gas-phase tests of this catalyst showed bulk activity similar to the Co based catalyst at 26.7 mols syngas/kg cat/hr (Table 12), but with a high specific activity of 0.48 mol CO/mol Ru/min. Methane selectivity was somewhat high at 19%, at the expense of fuel range hydrocarbons, which were approximately 10% lower than the basecase Co catalyst. Slurry-phase activity of this Ru/Zr/Al_2O_3 catalyst was significantly lower than the gas-phase activity as shown in Table 12. Fairly rapid deactivation of the catalyst was observed in the slurry reactor.

Since a silica support provided an improvement in activity for the Co based catalyst, it was examined with the Ru/Zr catalyst in gas-phase tests. At 240°C, this Ru/Zr/silica catalyst gave 49% syngas conversion with bulk activity of 70.7 moles syngas/kg cat/hr and specific activity of 0.834 moles CO/mole Ru/min. At 260°C, syngas conversion increased to 56% with bulk activity and specific activity both increasing to 81.1 moles syngas/kg cat/hr and 1.05 moles CO/mole Ru/min, respectively. When compared at the same temperature of 260°C, this 4.0% Ru/Zr/silica catalyst had triple the bulk activity and double the specific activity of the 2.87% Ru/Zr/alumina catalyst.

The water-gas shift activity of this Ru/Zr/silica catalyst was low as indicated by comparing the feed ratio, which was 1, to the observed usage ratios of 0.45, 0.39 and 0.46 at 220, 240 and 260°C, respectively. This was similar to the shift activity observed on the alumina-supported Ru catalyst.

In general, the hydrocarbon selectivity of this Ru/Zr/silica catalyst was shifted toward higher molecular weight products. For gas-phase tests at 240°C, the C_{19+} fraction was 54% of the hydrocarbon product and at 260°C it decreased to 39%. This enhanced selectivity to wax is not unusual since Ru catalysts are used for the polymethylene synthesis(11). In that process, CO is hydrogenated over Ru metal at low temperature (100-140°C) and high pressure (1000 atm) to give 50-55 wt% solid wax having an average molecular weight of 15,000-20,000. Methane selectivity was low, especially for the gas phase reactor, and never was greater than 5.3%. The C_{2-4} cut was also small and at most accounted for 6.4% of the hydrocarbons. Because of this shift to heavy product, the straight-run liquid fuels fraction (C_{5-18}) was small (< 50%).

The performance of this Ru/Zr/SiO_2 catalyst in the slurry reactor was poor. After showing initial bulk activity of 43 moles syngas/kg cat/hr at 240°C the activity declined to 4 moles syngas/kg cat/hr after 280 hours on stream. This rapid deactivation of both Ru catalysts in the slurry reactor may be due to carbon deposition on these highly dispersed catalysts, thus blocking available active sites. Inactive carbon layers and carbon deposition have been observed in other studies of Ru catalysts.

Manganese was examined in a bimetallic catalyst system containing Co/Mn/Zr/Al_2O_3 in which the Mn was added as $Mn_2(CO)_{10}$. This catalyst was prepared using the improved preparation procedure in an effort to improve its performance over what was achieved in the previous contract. Gas phase test results showed its activity and selectivity to be similar to the basecase Co/Zr/Al_2O_3 catalyst; thus no effect of Mn was observed. Furthermore, some Mn was lost from the catalyst as volatile carbonyl species, which was found in the liquid product. Slurry testing was not performed.

Iron containing catalysts were also studied and are discussed in the next section.

3.1.10 Promotion of Water-Gas Shift Activity

The Co and Ru-based catalysts exhibit low activity for the water-gas shift (WGS) reaction, as reflected by their poor performance with CO-rich feeds. Figure 15 further illustrates this by comparing CO/H_2 usage ratios with feed ratios for the supported cobalt and ruthenium catalysts, as well as a precipitated iron catalyst, all in the slurry reactor. The cobalt catalyst showed the poorest CO usage at all feed levels; usage ratios never exceeded 0.60. The ruthenium catalyst offered some improvement with a usage ratio nearly matched to a CO/H_2 feed ratio of 1.0. The usage ratio, however, never improved above 0.9 as the feed ratio was increased. The slight improvement in shift activity for ruthenium correlates with its observed shift activity in homogeneous systems(12). Neither catalyst showed the excellent shift activity that is exhibited by precipitated or fused iron catalysts.

In an effort to improve the shift activity of the promoted Co on alumina catalyst, a commercially available, low temperature shift catalyst (Cu/Zn/Al_2O_3) was physically mixed with it and tested in the gas-phase reactor. The results are summarized in Table 13 along with results in which no shift catalyst was added. The added shift catalyst caused a drop in FT activity with no indication of enhanced shift activity. There was an increase in oxygenate production, especially of ethanol and higher alcohols. A second gas-phase test of the mixed catalysts, this time using preactivated shift catalyst, still gave lower FT activity than without shift catalyst, but shift activity increased slightly. Upon increasing the CO/H_2 feed ratio from 1.0 to 1.9, however, shift activity declined as the usage ratio dropped to 0.35.

Another approach toward improving the WGS activity of the Co catalysts was to add Fe to the composition. Initially, with the Al_2O_3-supported catalyst, this was done by using a mixed-metal carbonyl cluster containing Co and Fe. $FeCo_3(CO)_{12}/Al_2O_3$ was used without a promoter. Gas phase test results are shown in Table 14. Compared to the Co/Zr/SiO_2 catalyst, there was a 53% increase in the usage ratio; however, the bulk activity declined by 40%. Liquid fuels selectivity was enhanced by 22%.

Because of the enhanced activity provided by silica a mixed Fe/Co catalyst was prepared on this support with Zr promoter. There was only a 14% increase in the usage ratio over the basecase Co/Zr/SiO_2 catalyst, while bulk activity showed a slight decline. The addition of Fe apparently had no effect.

A catalyst containing only Fe was prepared to determine the inherent WGS activity assuming it would be reasonable. This Fe/Zr/SiO_2 catalyst showed very little Fischer-Tropsch activity over the entire 220°C to 280°C temperature range (<6% syngas conversion at 280°C). Loss of iron from the catalyst did not occur. The cause of the low activity may be due to formation of very small Fe particles which are known to exhibit low Fischer-Tropsch activity.

3.1.11 Extended Slurry Test

An extended slurry phase test (test #8862-1-31) was conducted for 4417 hours from December 1985 to June 1986. The three objectives of the test were: to check catalyst stability; to collect liquid fuel product and wax samples for characterization and upgrading studies; and to obtain data for kinetic studies. A silica supported Co/Zr catalyst (Catalyst #8466-31) was used because it had shown the best performance in previous slurry screening studies. The same catalyst charge was used throughout the test. The extended slurry test was carried out in a one liter reactor just as the slurry screening tests. Detailed descriptions of the extended slurry test and the supporting data can be found in the Oct-Dec 1985, Jan-Mar 1986, and Apr-Jun 1986 Quarterly Reports.

For the first 1012 hours of the slurry test, the reactor was run with the following conditions: temperature = 240°C, pressure = 300 psig, CO/H_2 = 0.5 mol. ratio, and space velocity = 1.8 L/g cat/hr.
During the course of the run, the bulk activity declined gradually

from 52.7 to 46.9 mol. syngas/kg cat/hr (Figures 16 and 17). Hydrocarbon selectivity was constant (Figure 18) and the usage ratio was equivalent to the feed ratio. The operation conditions for the next period from 1012 to 2188 hours on stream were: temperature = 260°C, pressure = 300 psig, CO/H_2 = 1.0 mol ratio, and space velocity = 2.0 L/g cat/hr. The results of this portion of the test were similar to those at 240°C. Specifically, there was a gradual decline in catalyst activity (Figures 19, 20 and 21). Liquid and wax samples were collected at both sets of conditions. Interestingly, the catalyst suffered no significant harm due to a power failure that occurred during the 240°C portion of the test (at 420 hrs-on-stream). All process characteristics such as activity and selectivity returned to the trend line when normal operation was restored 22 hours later.

At this point, after 2188 hrs, it was decided to attempt to obtain data that could be used for kinetic studies. Initially, the temperature remained at 260°C, but other feed conditions such as space velocity and CO/H_2 feed ratio were systematically varied according to a pre-determined matrix. Using the extended test conditions of temperature = 260°C, pressure = 300 psig, space velocity = 2.0 L/g cat/hr and CO/H_2 = 1.0 mol ratio as the basecase, the conditions were varied as follows:

CO/H_2 (mol ratio)	Space Velocity (L/g cat/hr)
0.5	1.8
0.5	1.0
1.0	1.0
0.75	1.5

Deactivation check runs were also made at baseline conditions.

A preliminary examination showed an apparent relationship between space velocity and the kinetic rate constant. To investigate this effect experiments were conducted in which the impeller speed was varied with constant feed conditions. This was done for each of two sets of feed conditions. In a separate test, gas velocity was changed by increasing the nitrogen feed. Total pressure was raised simultaneously in an attempt to maintain constant H_2 and CO partial pressure in the gas-phase and hence a constant solubility in the slurry-phase. An analysis of the results of the above tests indicated that mass transfer effects need not be considered in this operating region.

At 3964 hrs-on-stream the temperature was raised to 280°C for another series of kinetic experiments in which the CO/H_2 mol ratio and the space velocity were varied. These high temperature runs consistently produced high methane selectivities with the highest being 56.4 wt%. Two other items to note about the operation at 280°C were:

1) It was necessary to raise the reactor heat control unit to an unusually high temperature to maintain reactor temperature. Stabilizing the temperature had also become difficult.

2) The wax taps for these samples were yielding very small quantities of product. The highest calculated wax rate was 0.0018 g/min and the average was 0.0005 g/min. This compares to 0.0267 g/min for the last of the samples at 260°C.

The items noted above were probably related to an observation made after reactor shutdown. It was discovered that the "slurry" was a powdery substance resembling catalyst only and no liquid phase. The slurry oil may have been carried over as a mist. Alternatively, the equilibrium concentration in the gas phase leaving the reactor may have been greater than the fresh wax produced at the given reaction conditions. Note that the pure hydrogen feed for reactivation (see paragraph below) could have contributed to the latter effect. It is also conceivable that some of the heavier hydrocarbons were cracked to lighter products which would increase their volatility.

The last experiment prior to shutdown was to attempt to reactivate the catalyst. Pure hydrogen at 300°C and 300 psig was passed over the slurry bed for 66 hours. Hydrogen treatment was effectively used by the Germans to regenerate the commercial Co catalysts. The reactor was run at identical feed conditions before and after reactivation. The conversions were the same. The hydrogen reactivation test was greatly obscured by the total loss of slurry medium and the observed results were judged to be invalid.

Figures 22, 23 and 24 plot the performance at 260°C, $CO/H_2 = 1.0$, 2.0 L/g-hr and 300 psig over the entire run and show the gradual loss in activity, as well as the dramatic change in selectivity after running at 280°C during the 3964 to 4276 hrs-on-stream segment.

3.1.12 Catalyst Characterization

Another important objective of this study was catalyst characterization and its correlation to catalyst performance. X-ray photoelectron spectroscopy (XPS) was used to examine cobalt oxidation states; three spectra are shown in Figure 25. The lower spectrum is that for oxidized Co on promoted Al_2O_3 prepared from $Co(NO_3)_2$. The binding energy for Co 2p electrons of 781 eV corresponds to established values for Co(II) and Co(III). The strong interaction of cobalt with alumina was evident from the XPS data on fresh catalyst prepared from zero-oxidation-state $Co_2(CO)_8$. This data, shown as the middle spectrum, indicates that most of the cobalt is oxidized to 2+ and 3+. Only a shoulder corresponding to a binding energy less than 780 eV suggests the presence of a small amount of zero valent cobalt. Finally, upon activation in pure H_2 at 300°C, the top spectrum was obtained, indicating the presence of only oxidized cobalt.

The $Co_2(CO)_8/Zr/SiO_2$ catalyst, which was the best performing catalyst was also analyzed by XPS (Figure 26). Unlike the fresh $Co_2(CO)_8/Zr/Al_2O_3$ catalyst, the fresh silica catalyst showed no evidence of low oxidation state cobalt, only +2 and +3 valencies. These observations are somewhat surprising since silica is generally regarded as being less reactive than alumina toward metal carbonyls(13) and toward Co(14). Analysis of reduced $Co/Zr/SiO_2$ showed no indication of metallic Co (Figure 26A).

The XPS results seem to indicate a strong interaction between the metal and support. It is well established that supported cobalt, especially on alumina and at low loadings, is difficult to reduce(9). Hall and Meyers have used XPS to show that after H_2 reduction at 250°C, alumina-supported $Co_4(CO)_{12}$ had only 25% of its cobalt as zero valence(15). One factor that may have contributed to the present observations was the inability to do in-situ reductions on the electron spectrometer due to mechanical problems with the reactive atmosphere chamber.

Hydrogen chemisorption was used to determine active cobalt surface area and percent dispersion. The results, presented in Table 15, are consistent with the XPS observations in that only small amounts of metallic cobalt were available for H_2 adsorption. Active Co surface areas were $<10\ m^2/g$ and the highest dispersion was only 12%, obtained with the 11.0% $Co/Zr/SiO_2$ catalyst. The silica catalysts tended to have slightly higher Co surface areas and dispersions than the alumina catalysts. The $Ru/Zr/SiO_2$ catalyst had the largest total surface area, but metal surface area and dispersion was similar to the Co catalysts. Comparing the Co/Zr/silica catalysts having different Co loadings shows that total surface area decreased (as well as activity) with increasing loading. Metal surface areas and dispersions were enhanced at higher loadings but did not lead to an increase in activity. The values obtained for metal surface area and dispersion are similar to those reported in the literature for supported cobalt carbonyl catalysts(16). Chemisorption was performed at elevated temperatures because this is where the largest adsorption occurred.

3.2 Slurry Reactor Kinetic Studies

3.2.1 Olefin Incorporation

Mechanistic concepts were examined by studying the effects of adding ethylene to the feed. It has been postulated that light olefins, produced in the F-T synthesis, may be reincorporated into the surface carbon chain growth process, thus allowing for variations in selectivity. These experiments were performed at the end of the slurry screening test of the $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ catalyst (Run #7888-33-731, see Table 2), by adding 10 and 20 volume percent ethylene to the feed. The following four test conditions were conducted at 260°C:

Sample	P, psig	$CO/H_2/C_2H_4$ vol%	NL/g cat/hr
56	308	44/46/10	1.41
59	302	39/41/20	1.41
62	300	40/40/20	0.71
65	300	51/49/0	0.70
66	550	40/40/20	1.40

The major result of adding ethylene during samples 56, 59 and 62 was the production of ethane, as shown:

	Bulk Activity,	Hydrocarbon Selectivity, wt%						
Sample	mol syngas/kg cat/hr	C_1	C_2H_4	C_2H_6	C_{3-4}	C_{5-11}	C_{12-18}	C_{19+}
56	14.8	6.2	20.9	42.7	7.0	16.2	5.9	1.1
59	13.8	3.3	29.7	41.9	5.7	14.0	4.8	0.7
62	9.2	3.9	19.9	41.0	6.3	18.1	6.2	4.6
65	9.1	20.6	0.5	2.4	10.7	27.3	18.8	19.8
66	17.9	3.1	23.3	45.5	5.2	17.2	5.5	0.2

The rates of oxygenate production also increased, from 0.2 to 2.4 wt% of the total product yield, but with the majority of this fraction being propanol. No evidence of olefin reincorporation was observed in the FT product distribution other than hydrogenation of ethylene.

The process conditions were next returned to that of an earlier sample (#39, CO/H_2 = 0.98, 0.7 NL/g cat/hr) to determine the extent of catalyst deactivation before the high pressure operation with ethylene addition was investigated (sample 65). A 28% reduction in bulk activity was observed with methane selectivity at over 20 wt% compared with the 14.3 wt% of sample 39. The major product with ethylene addition and 550 psig was ethane (sample 66). A 23% increase in gasoline fuels, C_5-C_{11}, was observed compared to sample 59, but this was due mainly to a general shift in products into the heavier molecular weight region which is expected at high pressure. Compared with sample 59, the oxygenates selectivity increased from 1.49 to 2.06 wt%., again with mainly propanol production.

3.2.2 Kinetic Studies During Slurry Screening Tests

A kinetic data analysis program was developed to help determine the kinetic parameters of the catalysts tested in the laboratory reactors. The program correlated the rate of CO/H_2 consumption with the species concentrations at the catalyst surface, subject to the kinetic functionality chosen by the user. Henry's law was assumed to be valid for relating the liquid concentrations to the vapor partial pressures. The mass transfer from the bulk liquid to the solid surface was not rate determining (this was verified during the initial baseline slurry test conducted for this contract), thus surface concentrations are taken as identical to the bulk liquid values. The Henry's law correlations are based on regressions of data taken from a paper by Peter and Weinert(17). The liquid densities are calculated based on correlations proposed by Deckwer(18).

A summary of the program requirements and results are presented in Figure 27. The specifications include reaction stoichiometry and kinetics, the necessary reactor operation parameters, inlet conditions and observation data. The options include the choice of fixing or fitting kinetic parameters and regressing rate coefficients in a normalized or standard fashion. The kinetic rate expressions which were chosen for the program are summarized in Table 16.

The first set of slurry operation data to be analyzed by the kinetic analysis program was from a $Co_2(CO)_8/Zr/Al_2O_3$ catalyst similar to the basecase composition (see Table 2, run #8523-1-4). Two of the rate expressions outlined in Table 16 were needed to fit the data. The data at high H_2/CO feed ratios and high space velocities was best described by the first order rate equation (5),

$$-r_{CO+H_2} = kC^{a}_{H_2}C^{b}_{CO} \qquad (5)$$

where a = 1.1 and b = 0. The low H_2/CO data was fit more closely by equation (2),

$$-r_{CO+H_2} = \frac{k\ C_{H_2}}{1 + K\ C_{H_2O}/C_{CO}} \tag{2}$$

Where k = 0.349 and K = 0.425. This expression accounts for inhibition by water. The activation energy was in the range of 33-44 kJ/mole.

The data from the slurry screening test of the more active $Co_2(CO)_8/Zr/SiO_2$ catalyst was then analyzed by the kinetic program (see Table 2, run #8670-11-18). None of the kinetic expressions were fully able to describe the data. The best fit was provided by expression(2). This equation can be rearranged to give the following expression:

$$\frac{C_{H_2}}{-r_{CO+H_2}} = (K/k)(C_{H_2O}/C_{CO}) + (1/k)$$

Thus a plot of $(C_{H_2}/-r_{CO+H_2})$ versus (C_{H_2O}/C_{CO}) will be linear if this rate expression is valid. The data are plotted in Figure 28 for the 240°C, 260°C and 280°C samples. The limited set of data appear to fit the linear expression fairly well. From the intercept, the rate constant k is derived with the values ranging from 0.328 to 0.775 cc/g cat/sec. K is then determined from the slope and ranges from 0.466 to 0.302.

The Arrhenius plot of ln k vs. 1/T is shown in Figure 29. An activation energy of 51 kJ/mole was obtained from this plot. This is slightly higher than the range found for the alumina supported catalyst. The literature contains relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts (20-23), compared to the numerous studies with iron catalysts. From this available literature, the range of activation energies for cobalt catalysts was 67-117 kJ/mole and 37-105 kJ/mole for iron catalysts. None of these catalysts were prepared from metal carbonyls nor studied in a slurry phase reactor. Our activation energies for metal carbonyl derived catalysts are significantly lower.

3.2.3 Extended Slurry Test Kinetic Studies

The data obtained from the extended slurry test of the $Co/Zr/SiO_2$ catalyst (run #8862-1-31) was analyzed to determine if a kinetic functionality could be established. The analysis was performed using the kinetic analysis program described above. The available kinetic expressions were those outlined in Table 16. Impeller speed tests, as described in section 3.1.11, were done to determine that mass transfer effects were not obscuring the kinetic measurements.

The next step was to account for the catalyst deactivation that had occurred during the experimental period of interest. Fortunately, a preliminary analysis of catalyst deactivation showed it to be relatively uniform for the 260°C runs, so a linear deactivation profile, was assumed. For a given kinetic rate model, the catalyst activity can be plotted against time to obtain the activity. The calculated activity rate can be used to adjust the raw reaction rate for each individual sample to a fixed point in time. The adjusted data is used in the computer model to solve for the intrinsic kinetic constants.

Table 17 displays the kinetic parameters derived from the non-linear regression on eqs. 1, 2, 4 and 5 (Table 16). The results for eq. 3 are not included because it was found that the best fit for parameter K_2 in eq. 3 was 0. Thus, eq. 3 became identical to eq. 1 and was eliminated from further consideration.

While all four of the kinetic models result in an adequate representation of the data, model 4, which includes the water inhibition effect, provides the best fit. The average error of 6.2% for model 4 (see Table 17) is the smallest of the four models. The linearized plot (Figure 30) and parity plot (Figure 31) for model 4 show a good fit over the entire range of data collected at 260°C. Figure 32 shows the relative deactivation that occurred, as determined by using model 4. Interestingly, this model has been shown by other investigators(24) to describe data with high water concentrations quite well. The low water-gas shift activity of the Co catalyst resulted in high water concentrations in these experiments.

The model with the second best average error was model 5. This model fit the data quite well in the mid-range but drifted at the extremes, especially at the high values of rate. Extrapolation could be a serious problem with this model. The rate constants obtained for model 4, based on fresh catalyst activity, are $k = 5.24 \times 10^9$ exp

(-23254/RT) cc/g cat/sec and $K = 1.55 \times 10^{-3} \exp(-6250/RT)$ mol/cc. The Arrhenius plot is shown in Figure 33 and the activation energy is found to be 97 kJ/mole, which is more in line with the reported values for Co-based catalysts(20-23).

3.3 Fuel Product Characterization

Two sets of liquid organic and wax products were collected during the extended slurry test of the $Co_2(CO)_8/Zr/SiO_2$ catalyst (Test #8862-1-31). These products were collected in order to isolate and characterize the diesel fuel fraction. The first set of products was collected during the initial 1000 hours of operation during which the reactor conditions were: 240°C, $CO/H_2 = 0.5$, SV = 1.8 L/g cat/hr and 300 psig. The diesel range product (C_{12}-C_{19}) contained in the wax from this sample was isolated by vacuum distillation and combined with the one gallon of liquid organic product. The wax contained 9 wt% diesel product. The combined sample was then fractionated by vacuum distillation with the diesel product boiling range defined as 190°C to 338°C at 760 mm Hg (ASTM standard). The pot temperature was maintained below 240°C to prevent decomposition. A total of 1.06 kg of diesel range product was obtained.

The second set of liquid organic and wax products was collected during the second phase of extended operation where the conditions were changed to the following: 260°C, $CO/H_2 = 1.0$, SV = 2.0 L/g cat/hr and 300 psig. The diesel fraction was isolated in the same manner as before except that the diesel product contained in the wax fraction was not included.

The diesel fuel properties were determined by E. W. Saybolt and Company (Philadelphia, PA) using 11 standard ASTM tests. The results are shown in Table 18, along with the ASTM requirements for No. 1-D diesel fuel oil, which is the highest quality diesel fuel and is intended for uses requiring frequent speed and load changes. The FT diesel product falls within all the specifications except for viscosity, cloud point and the 90% boiling point. High values for these three properties indicate that the synthesized diesel product contains a greater concentration of heavier hydrocarbons. This diesel fuel falls well within all the specifications for the No. 2-D grade diesel fuel oil. The material has a fairly high flash point, essentially no water or sediment, low sulfur, and negligible ash and carbon residue. As a result of being this "clean", it is not corrosive. One outstanding property of the synthesized diesel fuel product is the high cetane value.

There was very little difference between the two sets of samples. The higher temperature and slightly higher space velocity during the second phase would tend to shift the hydrocarbon selectivity toward lighter products, but this was offset by the increased CO/H_2 feed ratio which would have the opposite effect. For reference, the ASTM requirements for all 3 grades of diesel fuel oil are listed in Table 19, as well as the ASTM copper strip corrosion test classifications, which are listed in Table 20.

A sample of wax (800g) from the second set of collected products was supplied to Signal/UOP Research Center for use in a DOE-supported project studying FT wax upgrading.