I. INTRODUCTION AND BACKGROUND

The goal of this project is the development of a commercially viable, cobalt-based Fischer-Tropsch (F-T) catalyst for use in a slurry bubble column reactor. Cobalt-based catalysts have long been known as being active for F-T synthesis. They typically possess greater activity than iron-based catalysts, historically the predominant catalyst being used commercially for the conversion of syngas based on coal, but possess two disadvantages that somewhat lessen its value: (1) cobalt tends to make more methane than iron does, and (2) cobalt is less versatile with low H_2/CO ratio syngas due to its lack of water-gas shift activity. Therefore, the major objectives of this work are (1) to develop a cobalt-based F-T catalyst with low ($<5\%$) methane selectivity, (2) to develop a cobalt-based F-T catalyst with water-gas shift activity, and (3) to combine both these improvements into one catalyst. It will be demonstrated that these catalysts have the desired activity, selectivity, and life, and can be made reproducibly. Following this experimental work, a design and a cost estimate will be prepared for a plant to produce sufficient quantities of catalyst for scale-up studies.

II. PROJECT DESCRIPTION

The Cobalt Fischer-Tropsch Catalyst Project is divided into five tasks designed to systematically develop catalysts through thorough investigation of influences of various promoters, additives, and supports on minimizing methane selectivity and increasing water-gas-shift activity.

Cobalt has long been known to be an excellent catalyst for the F-T synthesis. Nevertheless, all currently operating F-T plants feeding coal produced syngas use iron catalysts, in spite of the fact that cobalt-based catalysts have higher activity. Two factors that lower cobalt's value as a F-T

catalyst are its poorer selectivity, that is, it produces more methane and its inability to be used with low H2/CO ratio syngas because of its lack of water-gas shift activity. The broad objective of this proposal is to overcome these deficiencies.

In pursuing F-T catalyst development, there are several aspects that need to be considered. These are catalyst formulation, catalyst pretreatment, and catalyst performance. All of these aspects will be dealt with in this project.

In broad terms, the technical approach that will be used is outlined below.

a. Conduct a thorough review of the literature on F-T synthesis, both the journal literature and the patent literature. In this review, identify approaches for improving methane selectivity of cobalt-based catalysts, identify additives that have WGS activity, identify catalyst formulation options, and define critical pretreatment parameters.

b. Based on the above review, develop a list of catalyst formulations with potential for low methane selectivity and a list of catalyst formulations with potential for promoting the WGS reaction.

c. Screen these catalysts in a small, fixed-bed reactor. If no catalyst meets the target specifications, go back to step b. Otherwise, run catalysts that meet discrimination criteria in a slurry bubble column reactor.

d. Once catalysts with low methane selectivity and WGS activity have been identified, develop a catalyst combining both these functions and test as described above.

e. Having found catalysts that meet the desired criteria for activity and selectivity, optimize the pretreatment conditions.

f. Demonstrate catalyst reproducibility by having a commercial subcontractor prepare multiple batches for testing.

g. Demonstrate catalyst stability by running aging tests in a slurry bubble column reactor.

h. Based on above results, prepare a design for a plant to produce demonstration scale batches of catalyst. Develop capital and operating costs of this plant.

The program to carry out the above outlined work will consist of five major tasks:

Task 1 -- Catalyst Development

Task 2 -- Catalyst Testing

Task 3 -- Catalyst Reproducibility Tests

Task 4 -- Catalyst Aging Tests

Task 5 -- Preliminary Design and Cost Estimate for a Demonstration Scale Catalyst Production Facility

All aspects of the catalyst's role in F-T processing will be addressed, including catalyst preparation, pretreatment, and performance (activity, selectivity, and aging). In addition to gathering process data, the catalyst will be subjected to a number of analytical measurements at each stage to see how various treatments have affected the catalyst and its performance.

III. OBJECTIVES

The objective of this project is to investigate the influence of various promoters, additives, and supports on minimizing the methane selectivity and increasing the water-gas shift (WGS) activity of cobalt (Co) Fischer-Tropsch (F-T) catalysts. The ultimate goal of this investigation is

to identify and demonstrate a catalyst preparation procedure that will be scaled up for the reproducible synthesis of commercial quantities of supported CO catalysts with desired activity, selectivity, and lifetime for use in F-T synthesis in three-phase slurry bubble column reactors.

IV. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

TPR experiments using reduction with H_2 up to 900°C were carried out on the modified, alumina-supported Co catalysts in order to investigate the effect of the various promoters or modifiers (Ru, Pd, and Fe) on cobalt reducibility and extent of reduction.

The investigation of the effect of certain promoters (Fe, Pd, and Ru) on the deactivation characteristics of Co catalysts during F-T synthesis was continued during this reporting period. All catalysts were tested first at 220°C, then at higher temperatures from 240 to 280°C, while monitoring their deactivation.

The investigation of the deactivation characteristics of a selected number of Co catalysts using olefin hydrogenation and Boudouard reaction was completed during this period. Hydrogenation of isobutene (IB) was carried out in the presence of CO between 120 and 180°C and atmospheric pressure. CO dissociation activities of the catalysts were measured using a pulse technique at 2.5 atm and at temperatures between 180 and 280°C with intermittent H_2 bracketing at 350°C.

During this reporting period, a total of 9 runs were performed in the slurry bubble column reactor. Out of these 9 runs, 3 runs were carried out to evaluate the effect of certain promoters (Fe and Pd) on the deactivation characteristics of Co catalysts during F-T synthesis. The reaction was performed under standard conditions followed by high temperatures up to 300°C in

order to evaluate the catalyst resistance to deactivation. One SBCR run was carried out with a Co catalyst on alumina support that had been H_2 reduced and wax coated to evaluate this procedure for possible scale up for commercial applications. Another aging run was carried out successfully for ca.850 h using a Co/Al_2O_3.

A series of four SBCR runs was made with an iron catalyst supplied by DOE/PETC that had been used in the F-T Run II at Laporte, Texas. The F-T synthesis was carried out under similar or close to conditions used at Laporte in order to evaluate the catalyst performance and see wether some of the problem encountered during the Laporte run could have been predicted from a bench scale reactor run.

Four Co catalysts were run in a one liter autoclave at the Center for Applied Energy Research of the University of Kentucky, Lexington, Kentucky. Their performance in the CSTR was compared to the results obtained previously in the SBCR.

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. TASK 1: CATALYST DEVELOPMENT

a. Technology Assessment (Subtask 1.1)

Except for regular updating of the literature with the most recent publications, there was no activity during this period to report in this subtask.

b. Catalyst Formulation (Subtasks 1.2, 1.3, 1.4)

A list of all the catalysts formulated so far within Subtask 1.2 is given in Table 1 on page 19 with their compositions. No new catalysts were formulated or prepared during this period.

A list of all the catalysts formulated so far within Subtask 1.3 is given in Table 2 on page

25 with their composition.

c. Catalyst Characterization (Subtask 1.6)

Physical Properties

Table 3 on page 26 gives an update on the physical property measurements carried out so far. Nitrogen physisorption at 77 K was used to obtain surface area, pore volume and pore diameter of the calcined catalysts. Average particle size of the catalysts was determined using a Microtrac particle size analyzer.

Static Hydrogen Chemisorption

An updated summary of the properties of the Co catalysts as determined by H_2 chemisorption is given in Table 4 on page 30.

Temperature Programmed Reduction (TPR)

TPR experiments were carried out in an automated Altamira Instruments AMI-1 system. The procedure for these measurements was described in a previous quarterly report. All the TPR results obtained so far are summarized in Table 4 on page 30.

Figure 1 shows TPR traces obtained for the modified, alumina-supported Co catalysts during reduction with H_2 up to 900°C. The traces for the non-promoted and Ru only promoted catalysts (Co.005 and Co.053) are included for comparison purposes. Briefly, Ru was concluded to act as a reduction promoter by enhancing the reducibility at lower temperatures (note the shift of the reduction maxima by 100°C to lower temperatures), thereby increasing the total reducibility as well as the number of exposed metal atoms (see Table 4). In the TPR traces of Pd promoted Co catalysts (Co.067, Co.068) two low temperature reduction peaks at 70°C and at 164°C for Co.067 (137°C for Co.068) were observed. Additionally an intense peak at 370°C with expressed

tailing at higher temperatures was observed for Co.067. With higher Pd loading, the high temperature tailing was transformed into a broad reduction peak at 550°C extending beyond 700°C. In parallel, the peak at 70°C gained intensity whereas the second low temperature peak lost some intensity and was shifted somewhat to lower temperature. The total reducibility of the catalysts (<900°C) decreased with increasing Pd loading and was always lower than that of the Ru promoted ones. CoRuFe catalysts (Co.066 and CoW.10) exhibited one intense reduction peak at ca. 330°C. Additionally, the catalyst containing 10 wt% Fe exhibited a shoulder at 470°C. Although a low temperature shoulder at around 200°C was observed for Co.066, a separate low temperature peak as was the case with Ru or Pd promoted samples was not observed. With increasing Fe content the reducibility of the catalysts up to 900°C decreased.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

The investigation of the effect of certain promoters (Fe, Pd, and Ru) on the deactivation characteristics of Co catalysts during F-T synthesis was continued during this reporting period using Co.068, Co.069 and CoW.10. For this purpose, the reaction was initiated at the standard reaction temperature of 220°C (The standard reaction conditions and procedure used for testing most catalysts were described in previous quarterly reports) and allowed to proceed for ca. 20 h to reach steady-state. After dilution of the reactant stream with Ar (H_2/CO/Ar = 2/1/1), the temperature was increased to 280°C or another desired temperature over a period of 2.5 h and CO hydrogenation was continued at this new temperature for another 20-40 h. The performances of all these catalysts (highlighted in Table 5) at steady state are compared in Table 5 on page 34 with

those reported in the previous quarterly report. All the pertinent data (CO conversion, rates, product distributions, chain growth probabilities, Anderson-Schulz-Flory distributions, time-on-stream activity and Arrhenius plots when available) obtained with each run for each catalyst is given in Appendix A.

As indicated in the previous quarterly report, the deactivation process and rate for catalysts containing Pd or Fe (Co.066-Co.068) were similar to those of the alumina-supported catalysts tested previously (Co.005 and Co053), and none of the promoters helped to slow down the rate of carbon formation at high temperatures above 240°C. In addition, promotion with high loadings of Fe or Pd resulted in catalysts with relatively lower activity and higher methane selectivity. All these catalysts were tested as indicated, first at 220°C than at 280°C, while monitoring their deactivation. The only exception was Co.068 with 1% Pd which had adequate activity and selectivity as well as lower deactivation rate at the various temperatures tested (240, 260 and 280°C). Figures 2-14 illustrate the effect of temperature and time-on-stream on CO coversion and rates of total hydrocabon and C6+ formation for the various catalysts tested.

Co.069 with high Ru loading (2 wt%) did not show any improvement in performance over the catalysts with lower Ru loadings (0.5 wt%).

The investigation of the deactivation characteristics of a selected number of Co catalysts using olefin hydrogenation and Boudouard reaction was completed during this period. Hydrogenation of isobutene (IB) was carried out in the presence of CO between 120 and 180°C and atmospheric pressure. The reactant feed consisted of 7.1% IB, 28.3% H_2, 1% CO, with helium being the balance. The catalysts were reduced *in situ* in flowing hydrogen at 350°C for 10 h prior to reaction. After helium purge for 30 min, reaction was initiated at 120°C. In order to

limit the impact of deactivation, only two samples were taken at every temperature after 5 and 15 min on-stream and the catalyst was bracketed with H_2 for 30 min while raising the temperature. After having obtained data at the highest desired reaction temperature of 180°C, the catalysts were cooled to 120°C under H_2 and the hydrogenation activity was measured again. This procedure ensured that cumulative deposition of carbonaceous species on the surface did not occur since all catalysts gave identical hydrogenation rates at 120°C before and after determination of activation energies. Analysis of the reaction products was carried out with an on-line GC equipped with a packed column (0.19% picric acid on Carbosphere) and FID. Under our reaction conditions, no products other than isobutene, isobutane and methane were detected with all catalysts.

The results of the determination of the hydrogenation activity of the catalysts studied are compiled in Table 6 on page 40. During hydrogenation of isobutene in the presence of CO, isobutane was the only reaction product observed up to 160°C reaction temperature. At 180°C small amounts of methane were formed (<1%) which judging from the lack of other reaction products did not originate from hydrogenation of isobutene but rather from onsetting methanation of some dissociated CO. In the absence of CO, all catalysts showed complete conversion of isobutene to isobutane at 120°C. Promotion of Co catalyst with Ru doubled the hydrogenation activity at 120°C and more than tripled it at 180°C. Addition of Fe to CoRu almost completely reversed the effect of Ru as can be seen by the comparable values for Co.005 and Co.066 catalysts and was more expressed with increasing Fe concentration (CoW.10). The addition of Pd (Co.067, Co068), however, led to a dramatic increase in the hydrogenation activity by more than an order of magnitude compared with the plain Co catalyst and still by a factor of 8 compared with CoRu catalysts (Co.053 and Co.069). The apparent energies of activation measured for all the catalysts

were in the range of 90 kJ/mol and varied only subtly by about 7 kJ/mol suggesting a similar reaction pathway on all catalysts.

CO dissociation activities of the catalysts were measured using a pulse technique. A 1/4" stainless steel U-tube was used as reactor in which a 1/8" tube and a 1/8" thermocouple were inserted to reduce the void volume. Using an Altamira AMI-1 system, 500 μl pulses of CO in 72 cc/min He were contacted with 50-150 mg of the reduced catalyst at 2.5 atm and at temperatures between 180 and 280°C with intermittent H_2 bracketing at 350°C. The amount of catalyst used was adjusted to obtain approximately one monolayer coverage by one CO pulse with respect to the number of metal atoms exposed on the surface. The reactor effluent was continuously fed through a 3 ft Porapak-Q column which ensured separation of CO and CO_2. Detection was carried out with an on-line TCD. The rates of CO dissociation were calculated from the conversion of CO to CO_2 per pulse, assuming a contact time of the complete CO pulse with the catalyst according to the residence time of the pulse.

Table 7 on page 41 shows the results for the Boudouard reaction on modified Co catalysts. Since the rate of conversion decreased for subsequent CO pulses without intermediate H_2 bracketing only the first pulse was used for the calculation of rates. Although the accuracy of the data was generally satisfactory for Co catalyst the intrinsic low activity caused problems in determining the rate. Therefore, the rate was determined by averaging 5 CO pulses at each temperature between 240 and 260°C and extrapolating the value to the desired reaction temperature of 220°C using the Arrhenius equation. The data for Co catalyst, thus represent activities for a partially deactivated catalyst and exhibit a greater error due to the extrapolation. This may also explain the ca. 20 fold difference between the plain Co catalyst and the Ru

promoted ones. Based on this and the results for CoRu catalysts, the rate of CO_2 formation seems to correlate well with the amount of metal atoms exposed on the catalyst surface. Addition of increasing amounts of Fe to CoRu also gradually decreased the CO dissociation activity. The promotion with 1% Pd instead of Ru showed practically no influence on CO_2 formation. Using 2% Pd, however, reduced the CO dissociation activity by a factor of 2. The apparent energies of activation were around 106 kJ/mol $\pm$ 10 kJ/mol for all catalysts. This again suggests identical elementary pathways for CO_2 formation on all catalysts investigated.

b. Subtask 2.2 - Slurry Bubble Column Testing (SBCR)

1. Run Chronology

During this reporting period a total of 9 runs were performed in the SBCR's, Runs M3-48 through 53, plus Run 55 and M4-37,38. A chronology of the experimental runs performed in the two slurry bubble column reactors - M3 and M4 - is given in Appendix B. All comparisons of CO conversion and CH_4 selectivities discussed in this chronology were obtained from results obtained at the initial startup conditions -- 240°C temperature, 450 psi pressure, and 2/1 H_2/CO feed gas ratio.

A complete summary of all runs made in the M3-SBCR is given in Table I in Appendix C. Four tables of data were prepared in order to compare catalyst activities for Runs 2 to 50 in M3-SBCR at the same run conditions (see Tables II, III, IV, and V in Appendix C).

A complete summary of all runs made in the M4-SBCR is given in Table VI, Appendix C. Four tables were prepared to compare catalyst activities for Runs 3 to 38 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix C). A summary of all runs using catalysts made by Calsicat is given in Table XI, Appendix C.

Four catalysts were sent to the Center for Applied Energy Research of the University of

Kentucky at Lexington, Kentucky, and have been run in their one liter autoclave.The complete run results have been tabulated and are included in Appendix D along with a flow diagram of the autoclave system.

2. Discussion of Results

(a) Miscellaneous Runs Made to Evalute the Effects of Higher Temperatures on Selected Catalysts

One run was made with a catalyst containing 10% Co, 10% Fe, and 0.5% Ru on alumina support (see Run 48 in M3-SBCR in Table 8 on page 42). The CO conversion at startup conditions (240°C) was low, 8.5%, with a CH_4 selectivity of 10.8%, and THC production rate of 0.39 gm C_1+/gm cat/hr. The CO conversion jumped considerably after each temperature, but decreased to a lower level after 24 hours (see Figure 14). The THC production rate increased correspondingly with each temperature change (see Figure 15), while the CH_4 selectivity greatly increased with temperature (see Figure 16). The CO conversion dropped to 2.6% when the temperature was lowered to 240°C. This catalyst showed low resistance to deactivation at higher temperatures.

A second run was made with a catalyst containing 20% Co and 1% Pd on alumina support. The CO conversion was higher (26.7%) at startup conditions than the previous catalyst (see Run 49 in M3-SBCR in Table 8). The CO conversion and THC production rate peaked at 280°C and began to drop at 300°C (see Figures 17 and 18). The CH_4 selectivity continued to increase significantly, up to 60%, with temperature (Figure 19). The conversion dropped to 3.8% when returned to 240°C. This catalyst also showed low resistance to deactivation at higher temperatures.

A third run was made at these higher temperatures with a catalyst containing 15% Co, 5% Fe, and 0.5% Ru on alumina (see Run 50 in Table 8). The CO conversion at startup conditions was

21.1% with a CH_4 selectivity of 11.3%, which are both in the range expected for a 15% Co catalyst. The CO conversion and THC production rate peaked at 280°C and began to drop at 300°C (see Figures 20 and 21). The CH_4 selectivity increased at each temperature level and peaked at 42% at 300°C (see Figure 22). The CO conversion dropped to 3.2% when the reaction temperature was lowered to 240°C.

These catalysts are typical of other cobalt catalysts which have good initial catalytic activity, but deactivate fairly rapidly at reaction temperatures of 240°C and higher due to carbon or coke formation. Addition of Fe does not appear to help reduce the activity loss.

(b) Tests Made to Test the Laporte F-T Iron Catalyst in the SBCR

Four runs were made with an iron catalyst that was used in the F-T Run II at Laporte, Texas. The startup conditions and activation procedure for this iron catalyst are given in Table 9on page 43.

The first run, Run 51, was reduced in-situ as prescribed and the run conditions were changed to the baseline conditions: 175 psi pressure, 270°C reaction temperature, and a total gas feed space velocity of 3,335 sl/hr/Kg-Fe (see Table 10 on page 45). After 24 hours on-stream, the reactor temperature was raised to 300°C, the pressure to 600 psi (maximum pressure achievable in the SBCR), and the gas space velocity to 15,517 sl/hr/Kg-Fe. After 5 hours at these run conditions, the bottom reactor temperature rose to 437°C. Within 2 hours, the reactor plugged near the bottom just above the inlet filter. The run was terminated and the reactor was cleaned out.

A second run, Run 52, was charged and the catalyst was reduced in-situ the same as the previous run. Several run periods were made in which the temperature was raised from 270°C to 280°C, 290°C, and 300°C at 450 psi pressure and a total gas rate of 900 SLH with a H_2/CO ratio of 2/1 (see Table 11 on page 46). The reactor pressure was raised to 600 psi and then the H_2/CO ratio

was changed to 1/1. Within 2 hours, the temperature in the top section that contains the internal filter began to increase rapidly. The reactor heaters were turned off and the syngas flow was stopped, but the temperature increased above 350°C and the reactor plugged in the top section. The unit was shut down and cleaned out again.

A third run, Run 53, was charged and started the same as the previous two runs (see Table 12 on page 47). The base case conditions were the same as the previous two runs except the H_2/CO feed ratio was 1/1. Several run periods were made in which the temperature was raised from 270°C to 280°C, 290°C, and 300°C at 450 psi pressure and total gas rate of 900 SLH with the 1/1 H_2/CO ratio. The H_2/CO ratio was lowered to 0.7/1 and the reactor pressure was raised to 600 psi. Over a period of 4 hours, the reactor temperature gradually increased until it reached 360°C at which time the reactor plugged again in the top section near the internal filter.

The fourth run, Run 55, was charged with the same iron catalyst and reduced in-situ the same as the preceeding three runs. A total of four run periods were completed when the reactor plugged after the reaction conditions had been raised to 300°C and 500 psi (see Table 13 on page 48).

Synfluid was not fed continuously during any of the above four runs. Some synfluid was added daily to try to maintain the liquid slurry height in the reactor. Since there is no way to remove the heat of reaction except by changing the gas feed rates, there was little we could do to stop the reactor temperature from running away once it got started, particularly during the time the unit was unattended. It is obvious to us now that the heat removal capabilities of our unit had been exceeded, and the operation requires a technician on duty whenever the more severe operating conditions are reached so proper actions can be taken to prevent plugging of the reactor.

Table 14 on page 49 compares the most pertinent data obtain during the above iron catalyst

runs and the results obtained in Laporte with the same catalyst.

(c) Subtask 4.1 - Low Methane Catalyst Aging Studies

Run No. 37 was started in the M4-SBCR on August 14th with a charge of 25.0 gm of Catalyst No. Co.005. This catalyst is a base case catalyst containing 20% Co on an alumina support with no promoters. A complete summary of all the run conditions and results is given in Table 15 on page 50. Also, the CO conversion, THC production rate, and CH_4 selectivity vs. hours into run are plotted in Figures 23, 24, and 25.

The CO conversion at 215°C was too low, 8.0%, so the reaction temperature was raised to 220°C where the CO conversion leveled out at 14.4%. The THC production rate averaged 0.42 gm C_1+/gm cat/hr and the CH_4 selectivity was approximately 4.0%. The synfluid flow rate was stopped after 446 hours on stream. The CO conversion had decreased to 12.5% at this time, and the THC rate dropped to 0.36 gm C_1+/gm cat/hr while the CH_4 selectivity had increased to 5.0%.

At 449 hours, the N_2 feed rate was lowered from 62% to 40% of the total gas feed rate and the H_2 and CO feed rates were increased at a 2/1 ratio while maintaining the same total gas feed rate. The CO conversion dropped to 8.6%, but the THC production rate increased to 0.41 gm/gm/hr, and the CH_4 selectivity jumped to 10.4%. These conditions were held for 240 hours and the CO conversion dropped to 7.6%, the THC production rate to 0.36 gm/gm/hr while the CH_4 selectivity averaged 10.8%. The higher concentration of CO plus H_2 in the reactor tends to increase the CH_4 production rate.

At 663 hours on stream, the H_2/CO ratio was changed to 1.5/1 while maintaining the same total gas feed rate. The CO conversion dropped to 5.6%, THC production rate to 0.32 gm/gm/hr, and the CH_4 selectivity dropped to 8.4%.

The N_2 feed rate was lowered from 40% to 33% while maintaining the same total feed gas rate at 687 hours on stream. The CO conversion dropped again to 4.8%, the THC rate went down to 0.29 gm/gm/hr while the CH_4 selectivity rose up to 10.3%. The synfluid feed was restarted at 735 hours on stream. The CO conversion rose to 5.6%, the THC went up to 0.35 gm/gm/hr, and the CH_4 selectivity dropped to 8.6%. There is some beneficial effect of adding synfluid continuously during the operation. As seen above, reducing the N_2 concentration in the feed gas results in increased CH_4 selectivity.

At 759 hours the reaction conditions were returned to the initial conditions for Period 3. The CO conversion averaged 10.4%, the THC was 0.31 gm/gm/hr, and the CH_4 selectivity dropped to 4.7%. This was a loss of about 28% of the initial catalyst activity after 806 hours on stream.

The run was extended for one more day to check the catalyst activity at 33% N_2 feed rate at a 1.5/1 H_2/CO feed ratio. The CO conversion returned to about the same value, 4.5% vs. 4.8%, the THC to 0.28 gm/gm/hr vs. 0.29, and the CH_4 selectivities were similar, 9.7% vs. 10.3%. This run was shut down on September 18th after 830 hours of successful operation.

(d) Evaluation of Wax Coated Catalyst from Calsicat

Run No. 38 was made in M4-SBCR with a charge of a selected catalyst on alumina support that had been H_2 reduced and wax coated to evaluate this procedure. The catalyst activity was about 90 to 95% of a similar catalyst that had been H_2 reduced in a fluidized bed reactor and charged into the SBCR in a slurry protected under nitrogen (see Runs 33 and 38 in Table XI in Appendix C). The catalyst activity was much higher than three other batches of catalyst that were H_2 reduced and wax coated. Improvements were made in the H_2 reduction procedure. This procedure for reducing and inerting the catalyst would make it easier and more economical for charging large batches of catalyst

into a large commercial reactor.

3. Catalyst Recovery Analyses

The catalysts charged for all runs, except Runs 28, 30, and 33 in M3 and Runs 4, 20, and 29 in M4, have been recovered and the particle size distributions have been measured. The charge and recovered weights of all catalysts are given in Table 16 on page 51. The charge weights are in the H_2 reduced state while the recovered weights are in the oxidized state. Taking this into account, catalyst recoveries are quite good (greater than 90%). The mean volumetric diameters of both the charged and recovered catalysts with the calculated percent reductions in particle size are also given in Table 16. The particle size at the lower 10% pass-through point of the sample for both the charged and recovered catalysts are also given in Table 16.

A comparison of the mean volume diameters of the total feed and recovered samples shows that most of the alumina supported catalysts exhibited the least amount of particle size attrition (5 to 10%) during the reaction. The silica supported catalysts showed a 10 to 20% particle size reduction while a titanium supported catalyst had the highest reduction, 18.2% (see Run 8 in the M4-SBCR in Table 16.

Eleven catalysts prepared by Calsicat have been tested in the SBCR and the particle size reduction was very low, 0.5% for CAL.08 and 1.6% for CAL.05. All these catalysts were prepared on a Vista-B gamma-alumina catalyst support which has shown good resistance to attrition in the SBCR's.

If you compare the particle size of each sample of the 10% pass-through point, the increase in the amount of fines found in the recovered catalysts, as indicated by the lower particle size at the 10% point, is nearly proportional to the reduction in particle size obtained by comparing the mean

volume diameters of the charge vs. recovered catalysts (see Table 16). Since the particle size of the charge catalyst was determined on the catalyst after hydrogen reduction and air oxidation, we know that attrition occurred only during the SBCR reaction.

Subtask 2.3 - CSTR Testing

Four catalysts that had been sent to the Center for Applied Energy Research of the University of Kentucky at Lexington, Kentucky have been run in a one liter autoclave. A comparison of performance of these cobalt catalysts in the SBCR and CSTR is given in Tables 17 and 18 on pages 55-56. The complete selectivity and rate data are given in four tables in Appendix D.

The highest total flow rate which could be achieved in the CSTR was 5 Sl/min, i.e., one third of that used as a standard flow rate in the SBCR. Lower flow rates as low as 90 l/min were also tested in order to achieve maximum conversion (up to 99% CO conversion with CAL.13). A comparison of the data from both the CSTR and the SBCR (Tables 17-18) indicate that the CO conversion rates obtained with all the catalysts are within experimental error similar. These results indicate that the reaction in the SBCR was not mass transfer limited.

VI. PLANS FOR THE NEXT REPORTING PERIOD

Additional runs will be made in the SBCR in order to complete the evaluation of all the catalysts formulated for this project. The writing of the final report will be continued.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

The technical approach which has been proposed remains the same and all the tasks are proceeding within schedule.