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 H_2/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

Two new catalysts were formulated and prepared during this period under subtask 1.2. Three more catalysts were prepared by Calsicat for the reproducibility tests.

The characterization of all the catalysts in order to determine their physical properties (BET surface area, pore volume, pore size diameter, particle size distribution), as well as the cobalt reducibility, extent of reduction, and dispersion) was continued.

The investigation of the effect of pretreatment in various atmospheres (calcination in air or nitrogen prior to reduction in hydrogen, direct reduction without prior calcination, and reduction-oxidation-reduction (ROR)) of a selected number of catalysts was continued by completing their characterization following the different pretreatments.

Fixed-bed reactor testing of the catalysts was continued. Four new catalysts, including the three catalysts prepared by Calsicat, were tested for their F-T synthesis performance.

The effect of reaction temperature on the performance of Co catalysts during F-T synthesis was investigated in the fixed-bed reactor using a low activity catalyst and one of the most active catalysts in order to determine their deactivation behavior.

During this reporting period a total of 11 runs were performed in the slurry bubble column reactor. Out of these 11 runs, three were high CO conversion runs, three were reproducibility

tests using the Low methane selectivity catalysts prepared by Calsicat, and the others were miscellaneous runs made to evaluate the effects of various promoters.

A special test run was made in the M3-SBCR to determine whether slugging or plugging occurred in the reactor system at higher solids loading.

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)

An updated list of all the catalysts formulated so far within Subtask 1.2 (including those catalysts listed in previous quarterly reports) is given in Table 1 on page 17 with their compositions. The last column of Table 1 indicates whether the catalyst has already been prepared. Of the 83 catalysts listed in Table 1, two new Co catalysts (highlighted in Table 1) were formulated and prepared in-house during this period and three others (CAL.11-CAL.13) were prepared by Calsicat. The detailed formulations of the new catalysts are given in Appendix A.

Co.064 (with 20% Co, 0.5% Ru, and 8.5% Zr on alumina) and Co.065 (with 20% Co, 0.5% Ru, 8.5% Zr, and 0.3% K on alumina), were prepared this quarter in order to complete the investigation of the effect of ZrO_2 promotion on the catalytic properties of Al_2O_3-supported Co In F-T synthesis. Both catalysts were promoted with 8.5 wt% Zr which was first impregnated on the support prior to the Co impregnation, and Co.065 was also promoted with 0.3% wt% K.

Calsicat prepared three independent 1 kg batches (CAL.11-CAL.13) of a catalyst similar to Co.047 (with 20% Co, 0.5% Ru, and 0.3% K on alumina) which was selected as the low methane catalyst for the reproducibility test. The three catalysts were calcined in nitrogen.

Under Subtask 1.3 no new catalysts was prepared during this period. The list of the catalysts prepared previously is given in Table 2 on page 23 with their composition.

c. Catalyst Pretreatment (Subtask 1.5)

The investigation of the effects of pretreatment on the catalytic properties of a selected number of catalysts (Co.004, Co.015, and Co.055), all promoted with La_2O_3 and Ru or Re in the case of Co.055, was continued during this period by the characterization (mainly TPR and H_2 chemisorption measurements) of these catalysts following the different pretreatments. The effects of pretreatment in various atmosphere (calcination in air or in nitrogen prior to reduction in H_2, direct reduction in H_2 without prior calcination, and reduction-oxidation-reduction (ROR) were addressed. The results are included in subtask 1.6, "Catalyst Characterization".

d. Catalyst Characterization (Subtask 1.6)

Physical Properties

Table 3 on page 24 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 27. Co.004, Co.015, and Co.055 were characterized by static hydrogen chemisorption at the University of Pittsburgh following different pretreatments.

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 27. During this period, Co.004, Co.015, and Co.055 were characterized by TPR following different pretreatments.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

The reaction conditions and procedure were described in previous quarterly reports. Four (4) new catalysts (Co.061, CAL.11-CAL.13) were tested for the first time during this reporting period. Catalysts Co.005 (runs #8-10c), Co.053 (run #7-11a) were also retested in order to investigate the effect of reaction temperature on the Co catalysts deactivation during F-T synthesis and determine the cause of such deactivation.

The performances of all these catalysts (highlighted in Table 5) at steady state are compared in Table 5 on page 31 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 B.

Co.061, a Ru-promoted Co catalyst with 30% Co loading was tested as part of an ongoing study of the effect of Co loading. As the results indicate, the Ru promotion results in a two-fold increase in activity from that obtained with the non-promoted catalyst, Co.060, reported in the previous report.

The three catalysts prepared by Calsicat (CAL.11-CAL.13) for the reproducibility study were tested in the fixed bed reactor. Their performances for F-T synthesis were similar, and they were also similar to the performance obtained with Co.047 under the same reaction conditions.

In previous runs, most of the highly active catalysts deactivated promptly as soon as they were subjected to relatively high temperatures resulting from excessive and uncontrolled release of the heat of reaction. Thus, the effect of reaction temperature on the performance of Co catalysts during F-T synthesis was investigated using a low activity catalyst, Co.005, and one of the most active catalysts, Co.053. The catalysts were tested at various temperatures while monitoring their deactivation. In most cases, the catalysts were diluted with alumina and the reactants with argon in order to avoid any uncontrolled temperature increases due to the heat released by the reaction at high temperature. It is clear from these preliminary results that Co catalysts are very sensitive to temperature. They deactivate very fast at temperatures above 240°C. Further discussion of these results will be left until the completion of this study by other tests which are required in order to determine the nature of this deactivation process and the means to prevent it.

b. Slurry Bubble Column Reactor

1. Run Chronology

During this reporting period a total of 11 runs were performed in the SBCR's, Runs M3-35 through 39, and M4-28 through 33. A chronology of the experimental runs performed in the two slurry bubble column reactors - M3 and M4 - is given in Appendix C. 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 in the M3-SBCR is given in Table I in Appendix D. Four tables of data were prepared in order to compare catalyst activities for Runs 2 to 39 in M3-SBCR at the same run conditions (see Tables II, III, IV, and V in Appendix D).

A complete summary of all runs made in the M4-SBCR is given in Table VI, Appendix D. Four tables were prepared to compare catalyst activities for Runs 3 to 33 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix D).

2. Discussion of Results

a. High CO Conversion Runs

Three high CO conversion runs were made during this reporting period. Two runs were made with a larger charge of catalysts, and one run was made with a normal charge of 15 gm of catalyst.

Run No. 35 in the M3-SBCR was started with a charge of 26.0 gm of Catalyst No. Co.041. This catalyst contained 20% Co plus 8.5% Zr and 0.5% Ru on silica support. The CO conversion was 35.7% at startup conditions and increased to 42.1% at 250°C, and 45.1% at 260°C reaction temperature (see Table 6). Lowering the total gas feed rate from 905 SLH ("standard liter per hour") to 544 SLH resulted in a slight increase in CO conversion to 46.7%, and lowering the feed gas rate to 403 SLH increased conversion to 49.6%. Reducing the N_2 feed rate to 40% of total with a corresponding increase in H_2 and CO rates reduced the conversion to 47.9%. Reducing the N_2 feed rate to 25% increased the conversion back to 49.7%. Returning the reactor to startup conditions resulted in 19.6% CO conversion, about one half of the initial activity. The

activity loss probably occurred at the higher temperatures. The CO conversions for this run were similar to previous high conversion runs.

Run No. 29 in M4-SBCR was started with a charge of 45.4 gm of Catalyst No. Co.061 (30% Co with 0.5% Ru on alumina support). The initial CO conversion was 42%, but slowly diminished to 29% over a 24-hour period. Catalyst was found in the overhead product for the next three days. The run was shut down and the reactor was drained without flushing. The reactor walls and internal filter were clean on the surfaces. The internal filter pores were filled with wax and catalyst which was easily removed by steaming. The internal filter will be cleaned more thoroughly after each run until the optimum catalyst loading that can be used in the existing SBCR's has been determined.

Run No. 30 in the M4-SBCR was started with a charge of 15.9 gm of catalyst No. Co.011, an unpromoted 20% Co on silica supported catalyst. The CO conversion was only 8% at startup conditions. The CO conversion increased as the reaction temperature was increased to 280°C and the feed gas rates were reduced, but never exceeded 38.5% (see Table 7). This run may be repeated at a higher catalyst charge level.

Further attempts to operate at higher CO conversions will be made during the next reporting period as soon as new catalysts are prepared.

b. High Catalyst Charge Run to Evaluate Slugging and Plugging in the SBCR Reactor System

A special test run was made in the M3-SBCR to determine whether slugging or plugging occurred in the reactor system at higher solids loading. A charge of 50 wt% inactive catalyst in synfluid was charged to the M3 reactor. The reactor was brought up to 240°C, 450 psi, and 900

SLH nitrogen gas feed rate. No catalyst carryover was observed. The gas rate was increased to 1300 SLH with still no solids carryover. Finally synfluid was fed at 30 ml/hr and no overhead slugging and no plugging occurred in the internal heavy product filter. The reactor system can handle high solids loading. However, the reactor cannot handle high heat generation because there is no capability for removing the heat of reaction except by lowering the inlet gas temperature and by adding more nitrogen in the feed gas.

c. Miscellaneous Runs Made to Evaluate the Effects of Various Promoters

One run was made with a catalyst containing 20% Co, 1.0% Re, and 1.0% La_2O_3 on silica support (see Run 28 in M4-SBCR in Table 8). The conversion is very similar to that obtained with an unpromoted silica support catalyst, Co.011 (see Run 9 in M3-SBCR in Table 9). Addition of Re and La_2O_3 does not improve catalyst activity on either silica or alumina supports.

One run was made with a catalyst containing 20% Co and 8.5% Zr on alumina support prepared with aqueous IW coimpregnation. The initial CO conversion was 24.0% (see Run 36 in M3-SBCR in Table 9). This was about 3.5% lower than obtained in multiple steps, aqueous IW, with Zr pre-impregnation (see Run 15 in M4-SBCR in Table 8).

One run was made with a catalyst containing 20% Co and 4% Zr on silica support (see Run 32 in M3-SBCR in Table 9). Conversion was only 14.8% at startup conditions which was at least 4% lower than obtained with similar catalysts containing 0.0, 0.7, 8.5, and 15% Zr (see Runs 9, 17, 19, and 32 in M3-SBCR on Table 9). There is something wrong with this catalyst and the run should be repeated.

Run 38 in M3-SBCR was made with a catalyst containing 20% Co plus 1% La_2O_3 on alumina support. The CO conversion at startup conditions was 28.0% which was nearly identical to that obtained with Catalyst No. Co.005 which contained 20% Co and no additives (see Run 15 in M3-SBCR in Table 9). The addition of a small amount of La_2O_3 had no effect on catalyst activity.

The last run made this period to test the effects of various promoters was made with a catalyst that contained 20% Co with 0.5% Ru and 8.5% Zr on alumina support (see Run 39 in M3-SBCR in Table 9). The CO conversion and CH_4 selectivity was almost identical to that obtained with Catalyst No. Co.053 which contained 0.5% Ru and no Zr (see Run 12 in M4-SBCR on Table 8). The addition of Zr to promoted or unpromoted alumina catalysts has little or no effect on catalyst activity.

The following conclusions can be made on the effects of adding various promoters based on the preceding experiments:

- The addition of Re and La_2O_3 on silica supported catalysts does not improve catalyst activity.
- Aqueous IW coimpregnation of Zr on alumina supported catalyst appears to yield lower activity than preparation of catalyst in multiple steps using aqueous IW with Zr pre-impregnation.
- The addition of 1% La_2O_3 on alumina supported catalyst had little effect on catalyst activity.
- The addition of Zr to promoted and unpromoted alumina catalysts has little or no effect on catalyst activity.

c. Subtask 3.1 - Reproducibility of Catalyst with Low Methane Selectivity

Three 1 Kg samples were obtained from Calsicat for reproducibility and aging tests. Each catalyst contained 20% Co, 0.5% Ru, and 0.3% potassium on Vista Catapal B alumina.

Run No. 31 in the M4-SBCR was started with a charge of Calsicat Catalyst No. CAL.12 (see Table 10). The initial CO conversion at startup conditions was 27.6%, the THC production rate was 1.26 g C_1+/g cat./hr, and the CH_4 selectivity was 7.9%. These values are very similar to those obtained with two previously formulated Calsicat catalysts, CAL.03 and CAL.05, and to the reference catalyst prepared by Pitt, Catalyst No. Co.047 (see Runs 16, 19, 31 in M4-SBCR and Run 23 in M3-SBCR on Table 10).

The other two Calsicat catalysts, Nos. CAL.11 and CAL.13, yielded similar CO conversions and production rates (see Runs 32 and 33 in M4-SBCR on Table 10). Run 33 will be extended up to 1000 hours at the same run conditions as the catalyst aging test of the low methane selectivity catalyst prepared by Calsicat. At 111 hours into the run, the CO conversion had dropped from 28.1% to 25.12% and the THC production rate from 1.28 g/g cat./hr to 1.15 g/g cat./hr. For the next 400 hours the CO conversion slowly dropped at 0.6% per day to 17.2% and the THC production rate dropped at 1.1 g/g cat./hr. This run will be continued to 1000 hours on stream as scheduled.

3. Catalyst Recovery Analyses

The catalysts charged for all runs, except for 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 11. 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 11. 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 11.

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 11).

Nine 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 11). 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.

VI. PLANS FOR THE NEXT REPORTING PERIOD

Several tasks are planned for the next reporting period:

(a) The fixed-bed reactor testing of new catalysts will be continued.

(b) The systematic characterization of all the catalysts will be continued using the following techniques:

- Selective hydrogen chemisorption on the reduced catalysts at 100°C;
- X-ray diffraction before reduction, after reduction, and after slurry bubble column reaction;
- Temperature programmed reduction (TPR);

(c) The investigation of the effect of temperature on catalyst deactivation will be continued.

(d) New catalyst formulations will be generated in order to pursue the effect of certain promoters on catalyst deactivation.

(e) Additional runs will be made in the SBCR's to maximize the CO conversion.

(f) Reproducibility tests and aging runs will be made on catalyst obtained from Calsicat.

(g) Several catalyst formulations and mixtures will be tested for water-gas shift activity.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

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