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

Eight new catalysts were prepared by Calsicat during this period following the formulations used previously for Co.005 and Co.047. The main differences between the catalysts in each of these two catalysts series reside in the reduction and passivation procedures used.

TPR experiments were carried out on both promoted and unpromoted catalysts in order to determine the optimum time required for complete catalyst reduction.

During this reporting period, a total of 8 runs were performed in the slurry bubble column reactor. All these run were carried out in order to evaluate the reduction procedure which would be used on large batches of catalysts as well as the passivation procedure using soya wax coating of the Co catalysts after reduction in H_2 for possible scale-up for commercial applications.

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

11 with their compositions. Eight new catalysts were prepared by Calsicat during this period following the formulations used previously for Co.005 (CAL.15-CAL.17, CAL.19-CAL.20, and CAL.24) and Co.047 (CAL.18 and CAL.25). The main differences between the catalysts in each of these two catalysts series reside in the reduction and passivation procedures used for each one.

These new catalyst preparations resulted from discussions between EI and Calsicat which revealed a number of critical scale-up problems associated with the pretreatment and the handling of Co catalysts in reduced state.

One of the problems was encountered when three large batches of the non-promoted catalyst (CAL.15-CAL.17) equivalent to Co.005 were prepared by Calsicat and reduced under semi-commercial conditions and passivated in soya wax. All three catalysts showed very low activity. In order to ascertain that the low activity was not due to the preparation procedure, or the waxing process used at Calsicat, other pretreatment conditions were tried using calcined batches of the same catalysts supplied by Calsicat. CAL.19 was reduced in a small batch at EI in the laboratory scale reduction system using the same conditions that resulted in the very active Co.005 catalyst. CAL.20 was also reduced at EI but in a larger batch in order to simulate the conditions used at Calsicat. Following the low activity result obtained with CAL.20, CAL.24 was obtained by rereducing twice CAL.20, but this time in a smaller batch and similar conditions to those used for CAL.19.

CAL.18, a Ru promoted catalyst, was prereduced in a large batch at Calsicat and protected in soya wax. CAL.25 is a small batch of the same catalyst as CAL.18 which was shipped in the calcined state and reduced at EI under standard conditions for comparison purposes.

c. Catalyst Characterization (Subtask 1.6)

Temperature Programmed Reduction (TPR)

TPR experiments were carried out in an automated Altamira Instruments AMI-1 system in order to determine the optimum time required for complete catalyst reduction. The reduction time and the corresponding H_2 consumption may add asignificant amount to the overall cost of the catalyst. The catalyst tested were the non-promoted catalyst Co.005, the Ru-promoted catalyst Co.053 and the Ru-K-promoted catalyst CAL.13.

A first TPR is carried out from ambient temperature to 350°C under 10% H_2 in argon. The temperature is then maintained at 350°C for the time required for "normal" reduction (different times were tried: 2 h for all catalysts and 4,10, and 16 for Co.005). The catalyst is then cooled to ambient temperature and a second TPR is then performed up to 900°C to determine the amount of catalyst remaining unreduced after the 350°C reduction. The reducibility results are shown in Table 2 on page 17. These results confirmed previous results showing that Ru acts mainly as a reduction promoter. In addition, the presence of potassium did not alter its effect on Co reducibility. It is also clear from these results that much longer time (at least 16 h) is required for the non-promoted catalyst to achieved its maximum reduction.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

This subtask was completed in the previous period.

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

1. Run Chronology

During this reporting period a total of 8 runs were performed in the SBCR's, Runs M3-60, 61, and 62, and Runs M4-42, 45, 47, and 48. A chronology of the experimental runs performed in the two slurry bubble column reactors - M3 and M4 - is given in Appendix A. All comparisons of CO conversion and CH_4 discussed in this chronology were obtained from results obtained at the following reaction conditions: 220°C temperature, 450 psi pressure, 2/1 H_2/CO feed gas ratio. and 900 SLH total gas flow.

A complete summary of all runs made in the M3-SBCR is given in Table I in Appendix B. Four tables were prepared in order to compare catalyst activities for Runs 2 to 62 in M3-SBCR at the same run conditions (see Tables II, III, IV, and V in Appendix B).

A complete summary of all runs made in the M4-SBCR is given in Table VI in Appendix B. Four tables were prepared to compare catalyst activities for Runs 3 to 48 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix B).

2. Discussion of Results

(a) Evaluation of Wax Coated Non-Promoted Catalysts from Calsicat

Three SBCR runs were carried out during this period using catalysts prepared at Calsicat following the successful formulations used for Co.005 previously prepared and tested at EI. The catalysts (CAL.15-CAL.17) were calcined and reduced at Calsicat under semi-commercial conditions and flaked in soya wax for easier handling and shipment of the reduced catalysts. All catalysts yielded 2.0% CO conversion or lower (see Runs 3060, 3061, and 4042 in Table 3 on page 18). In order to assess the reason for such low activity a small batch of the same catalyst was shipped in the dry, calcined state and H_2 reduced in EI's laboratory scale reduction column (CAL.19). This catalyst was very active yielding 13.6% CO conversion (see Run 3062 in Table 3). This result indicate that the actual formulation and preparation of the three catalysts CAL.15.

CAL.16 and CAL.17, up to their calcination were not the cause of their low activity. Thus, it was necessary to investigate the effect of the reduction procedure as well as the passivation process used by Calsicat.

Another batch of the same non-promoted Co/Al_2O_3 catalyst (CAL.20) received from Calsicat was hydrogen reduced in our laboratory scale reduction unit. However, a batch of 220 g, larger than ussually used, was charged this time to the reduction unit and was reduced at standard conditions: 350°C for 18 hours with 5 SLM H_2 flow rate. The resulting CO conversion was only 3.4% (see Run 4045 in Table 3). This result indicate that the wax coating method of passivating the reduced Co catalysts was not the cause for their low activity. About 100 g of this reduced catalyst was re-reduced twice at the same conditions (CAL.24). The CO conversion only increased to 4.9% (see Run 4047 in Table 3). The results indicate that the H_2 reduction of non-promoted Co/Al_2O_3 catalysts is more difficult than for promoted catalysts and only small batches can be completely reduced in our laboratory reduction column at standard conditions. In addition, the larger batch semi-commercial reduction process seemed to have irreversibly damaged this catalyst which could not be reduced completely even when the re-reduction was carried out in small batches at standard conditions yielding usually completely reduced catalysts . The large amount of water produced during reduction of large batches of catalysts is suspected to affect the reducibility of these non-promoted catalysts. Further tests which will be carried out during the next reporting period in order to elucidate this problem.

(b) Evaluation of Wax Coated Promoted Catalyst from Calsicat

Run No. 4043 was made in M4-SBCR with a Ru-promoted catalyst from Calsicat (CAL.18) that was hydrogen reduced and coated with soya wax. A similar catalyst (CAL.25) that was reduced at EI and charged in Synfluid was run at the same conditions. The wax coated catalyst yielded a CO conversion of 8.4% vs. 9.5% for the uncoated catalyst (see Runs 4043 and 4048 in Table 3). The catalyst activity was much higher than that of previous batches of wax coated catalysts, but further improvements in this passivation procedure are needed. None of the problems encountered with the reduction and passivation of the non-promoted catalysts were observed with these promoted catalysts, confirming again that the presence of Ru promotes the reduction of the Co catalysts.

C. TASK 5: CATALYST PREPARATION FACILITY

The objective of Task 5 was redefined in agreement with the Program Manager. The new objective of Task 5 is the cost estimate for the preparation of commercial quantities of the best catalyst identified in other tasks of this project. Formulation CAL-13 was chosen for the preparation of cost estimates by a catalyst manufacturer (Calsicat).

Discussions between EI and Calsicat have revealed a number of critical scale-up problems involving particularly the pretreatment and handling of Co catalysts in reduced state. Further SBCR testing using Co catalysts prepared by Calsicat and subjected to various pretreatments was required and undertaken during this reporting period (see Tasks 1 and 2) in order to address some of these issues.

VI. PLANS FOR THE NEXT REPORTING PERIOD

Additional runs will be made in the SBCR to complete the evaluation of the reduction procedure used for non-promoted Co catalysts. 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. Report writing is proceeding well but it is taking longer than anticipated due to the large volume of data. An extension was requested in order to complete any additional experimental work associated with Task 5 as well to complete all report writing.