I. EXECUTIVE SUMMARY

During the 8th quarter, a number of important steps have been taken and conclusions made.

Working with Calsicat on catalyst pretreatment and handling procedure, it was found that initial calcination in air vs. N_2 had little effect on the final catalyst properties. However, stabilizing a pre-reduced K- and Ru-promoted 20% Co/Al_2O_3 in paraffin wax was not sufficient for loading directly into the SBCR without re-reducing again. The catalyst may have sustained oxidation by oxygen diffusion through the wax or during the loading into the SBCR. It has been noted in the past that Co catalysts cannot be suitably reduced in-situ in the SBCR.

There is some evidence that direct reduction without calcination for some of the Co catalysts produces a more active catalyst. However, catalysts with higher initial activities appear to also be more susceptible to exotherming during startup, especially in gas phase reaction, with a concomitant loss of activity.

The Co catalysts being designed in this study particularly are required to have reasonably high activities and chain growth probabilities. In order to achieve this latter, catalysts must be able to operate at temperatures $<240°C$. As mentioned above, it has been noted that temperature surges during startup in the fixed-bed reactor lead to lower CO conversions. This effect of temperature on deactivating partially these catalysts has also now been seen in the SBCR.

To date, a potential support material ($CuCr/Al_2O_3$ has formulated which has very good water-gas-shift activity. However, fixed-bed results indicate that, when Co is loaded on this support, the resulting catalyst has both poor WGS activity and poorer F-T activity ($<50\%$).

When a physical mixture of Co/Al_2O_3 and the WGS catalyst $CuCr/Al_2O_3$ is used for reaction in the SBCR some WGS is evident which results in slightly higher activity and methane selectivity. However, the increase in CO_2 production is still not significant. Partly, this is a function of the relatively low temperature being used for F-T synthesis.

II. 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.

III. 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 pre-treatment 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 pre-treatment 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, pre-treatment, and performance (i. e. 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.

IV. 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.

V. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

Four (4) new catalysts were formulated and prepared during this period under both subtasks 1.2 and 1.3. Five more catalysts were prepared by Calsicat.

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.

Fixed-bed reactor testing of the catalysts was continued. Seven (7) new catalysts have been tested for their F-T synthesis performance. Some catalysts have been re-tested for reproducibility checks.

An investigation of the effect of pre-treatment (i.e. calcination in static air versus flowing air, direct reduction without prior calcination) of a selected number of catalysts upon their performance for F-T synthesis was continued during this period.

A paper comparing the effects of supports and promoters on the performance of Co F-T catalysts, both in fixed-bed and slurry bubble column reactors was presented at the 208th ACS

National Meeting in Washington, D.C., August 21-25, 1994.

Another paper comparing the performance of some of the patented Co F-T catalysts studied under this project was presented at the 11th Annual International Pittsburgh Coal Conference, September 12-15, 1994.

VI. 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 with their compositions. The last column of Table 1 indicates whether the catalyst has already been prepared. Of the 64 catalysts listed in Table 1, five (CAL.04-CAL.08) were prepared by Calsicat. Two (2) new Co catalysts (highlighted in Table 1) were formulated and prepared during this period. The detailed formulations of the new catalysts are given in Appendix A.

Co.055, an alumina-supported catalyst, is similar to Co.001, but without K. Co.056, a silica-supported catalyst, is similar to Co.025, but with La instead of Zr as a promoter. Both catalysts were formulated in order to investigate in more details the effects of certain promoters such as La_2O_3 and ZrO_2 which significantly affected the activity of cobalt for F-T synthesis in some of the previous formulations.

CAL.04-CAL.08 were formulated with the same composition as that of Co.047 which was selected as the low methane catalyst for the reproducibility test. The only difference between the various catalysts was in the pretreatment conditions (calcined only, reduced only, calcined and reduced, neutralized in air or in a paraffin wax). They were all prepared in small batches for formulation check and determination of the best pre-treatment to adopt for the

preparation of the larger batches to be used for the reproducibility tests.

Under Subtask 1.3 two catalysts were prepared. One Co catalyst (CoW.07), similar in composition to CoW.06, was prepared by pre-impregnating the silica with Cu-CrO and calcining this support precursor at 750°C, instead of 500°C used for CoW.06, before incorporating the cobalt. One water-gas shift catalyst, WGS.09, similar to WGS.03, a 5%Cu/4%Cr/Al_2O_3, which showed the best activity for water-gas shift, was prepared in a larger quantity in order to mix it with a cobalt catalyst for slurry bubble column testing of water-gas shift activity with F-T synthesis. The list of these catalysts is given in Table 2 with their composition, and the detailed formulations are included in Appendix A.

c. Catalyst Pretreatment (Subtask 1.5)

The investigation of the effects of pretreatment on the catalytic properties of a selected number of catalysts was continued during this period. The effects of calcination in static atmosphere versus flow, and the effect of reduction alone without prior calcination were addressed. The results are included in subtask 2.1 where catalysts calcined under different conditions were tested.

d. Catalyst Characterization (Subtask 1.6)

(1) Physical Properties

Table 3 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.

(2) Static Hydrogen Chemisorption

An updated summary of the properties of the Co catalysts as determined by H_2 chemisorption is given in Table 4. Metal dispersions and particle sizes of CAL.04-CAL.08 were determined by CO chemisorption carried out at Calsicat. Only three catalysts were characterized by static hydrogen chemisorption at the University of Pittsburgh because the system was still down and being repaired during most of this period. Co.005 was rerun for reproducibility check. Co.004 was characterized following two different pretreatments: one after calcination followed by standard reduction and the other after reduction only, without prior calcination. A high dispersion was measured for the latter.

(3) 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 the previous quarterly report. All the TPR results obtained so far are summarized in Table 4.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

(1) F-T Synthesis

The reaction conditions and procedure were described in the previous quarterly report. Seven (7) new catalysts (Co.032-Co.034, Co.055, CAL.04-CAL.06, UOP (F-T catalyst supplied by UOP)) were tested for the first time during this reporting period. Catalysts Co.05, Co.012, and Co.019, were retested to check the reproducibility of reaction results obtained previously for these catalysts. Co.004 (runs #2-5), Co.015 (run #2), Co.016 (run #2) , and Co.055 (run

#1-3) were also retested using different pretreatment procedures.

The performances of all these catalysts (highlighted in Table 5) at steady state are compared in Table 5 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.033 and Co.034 were tested in order to evaluate the effect of Zr promotion on Co/Al_2O_3. The results indicate that Zr enhanced significantly the activity of cobalt for F-T synthesis when it is pre-impregnated on the support.

Co.004 and Co.055 were tested both without and with calcination with air in a flow system prior to the standard reduction and reaction procedures. These catalysts, studied as part of the investigation of the effect of La_2O_3 promotion, had a very high activity, especially when they were directly reduced without prior calcination. The pretreatment environment (air vs. hydrogen) seems, therefore, to play a major role in the activation of these catalysts. Both catalysts, as indicated by the data reported for Co.004, run #2a, and Co.055, run #2, and as experienced with other highly active Co catalysts, were very sensitive to temperature effects during the reaction. Because of their high activity, a temperature surge was observed during startup of these runs, resulting in low activities.

The trial catalysts prepared at Calcicat, CAL.04-CAL.06, were all tested using the standard reaction conditions. They gave comparable results, irrespective of the pretreatment conditions used by Calsicat for the different catalysts. These results are also in agreement with those obtained with Co.047 which was prepared by PARC.

Catalysts Co.05, Co.012, and Co.019 gave slightly higher activities than obtained previously with the same catalysts. This is most probably due to the much improved analytical procedure used presently.

Co.005 (run #7) was tested in the second fixed-bed reactor system for reproducibility check between two different systems.

Co.015 and Co.016 were retested after calcination with air in a flow system. The data reported previously for these catalysts was obtained with the catalysts calcined in a "static" atmosphere at the University of Pittsburgh. As reported previously, this pretreatment procedure may result in low activity catalysts. The new results obtained for Co.015 and Co.016 calcined in flow show also higher activity than those obtained previously with the catalysts calcined in static air.

CoW.03-CoW.06, the catalysts formulated with a water-gas shift component, were also tested under F-T synthesis conditions and the results are included in Table 5. CoW.03 and CoW.04 had very low activity, while CoW.05 and CoW.06 had 50% lower activity than Co.005, a Co/Al_2O_3 catalyst. In addition, no significant effect on the water-gas shift activity was observed during F-T synthesis.

Co.005b and Co.005c, physical mixtures of an F-T catalyst, Co.005 (Co/Al_2O_3 catalyst), and a water-gas shift catalyst, WGS.03 ($CuCr/Al_2O_3$), were also tested under standard F-T conditions.

b. Subtask 2.2 Slurry Bubble Column Reactor Testing ("SBCR")

(1) Run Chronology

During this reporting period a total of nine runs were performed in the SBCR's, Run 29

in M3 and Runs 14 to 21 in M4. The following is a chronology of the experimental runs performed in the two SBCR's, M3 and M4. A comparison of the CO conversions and the product selectivities of the methane reduction catalysts at the initial operating conditions (i.e., 240°C temperature, 450 psi pressure, and 2/1 H_2/CO ratio) are listed in Tables 6 and 7. All comparisons of CO conversions and CH_4 selectivities discussed in the following chronology were obtained at the startup conditions.

Run No. 14 in the M4-SBCR was started on July 4th with a charge of 15.0 gm of Catalyst No. Co. 005 plus 5.0 gm of Catalyst No. WGS.03. This was a test run in which a cobalt-alumina based catalyst for methane reduction was mixed with a water gas shift catalyst. The CO conversion was slightly higher than using only Catalyst No. Co.005, 29.3% vs. 27.1%. The CH_4 selectivity was also higher, 10.1% vs. 7.9%. The CO_2 selectivity, however, was increased from 0.8% to 2.0%, an insignificant amount.

Run No. 15 in the M4-SBCR was started on July 18th with a charge of 13.0 gm of Catalyst No. Co.034. This catalyst contained 8.5% Zr on alumina support with no other additives. The CO conversion was the same as Catalyst No. Co.005, the alumina catalyst with no additives, 27.5% vs. 27.1%, but the CH_4 selectivity was higher, 10.4% vs. 7.9%. Adding zirconium to the Co-alumina based catalyst had no beneficial effect on lowering CH_4 production.

Run No. 16 in the M4-SBCR was started on August 1st with a charge of 16.1 gm of Catalyst No. CAL.04. This catalyst was supplied by Calsicat and contained 20% Co, 0.4% Ru, and 0.3%K. The CO conversion was 26.25% and the CH_4 selectivity was 7.1%. The CO conversion was about 2% lower than the same catalyst formulation, Co.047, which was prepared by Pitt.

Run No. 17 in the M4-SBCR was started on August 8th with a charge of 15.0 gm of Catalyst No. CAL.08. This catalyst was also supplied by Calsicat, but it was hydrogen reduced and encapsulated in paraffin wax. The catalyst was mixed with synfluid, heated to 100°C under a nitrogen blanket to make a slurry, and then transferred into the reactor under nitrogen. The CO conversion was only 16.9% with a 5.9% CH_4 selectivity. Some of the loss of catalyst activity may have been due to air diffusing through the wax coating during storage or while handling and charging it to the reactor.

Run No. 18 in the M4-SBCR was started on August 15th with a charge of 15.0 gm of Catalyst No. CAL.07. This was another Calsicat catalyst that was hydrogen reduced and encapsulated in paraffin wax. The catalyst charge amount was adjusted to compensate for the was content. The catalyst charge procedure was the same as that used for Run No. 17. The CO conversion was higher, 20.6%, with a corresponding increase of CH_4 selectivity, 7.3% vs. 7.1%.

Run No. 19 in the M4-SBCR was started on August 22nd with a charge of 15.7 gm of Catalyst No. CAL.05. This catalyst is identical to Catalyst No. CAL.04, except it was calcined in nitrogen instead of in air. The CO conversion was nearly identical to CAL.04, 26.6% vs. 26.3%, and so was the CH_4 selectivity, 7.3% vs. 7.1%.

An electrical storm occurred on August 27th and burned out the sequence board of the 5T.I. Programmable Logic Controller. Startup of Run No. 20 was delayed for one week to make the necessary repairs.

Run No. 20 in the M4-SBCR was started on September 5th with Catalyst No. CAL. 06. This was a Calsicat catalyst that had been hydrogen reduced and then stablized with air. The

purpose of running the stabilized catalyst was to see how much residual activity it may have even though it had been oxidized. The CO conversion was 5.6% at startup conditions and dropped to 3% at 220°C reaction temperature. This demonstrates that a reduced catalyst that has been stabilized with air has some residual activity.

Run No. 29 in the M3-SBCR was started on September 12th with 25.2 gm of Catalyst No. Co. 053. A larger amount of catalyst was charged to study catalyst loading and to obtain a higher CO conversion level. The initial CO conversion was the highest conversion obtained to date, 42.0% with a 16% methane selectivity. During Period 7 of the run, the syngas feed rate was reduced in half with a corresponding increase in nitrogen feed. The CO conversion dropped from 40.8% to 31.5%, which was due mainly to reducing the syngas partial pressure. The reaction conditions were returned to startup conditions, but the CO conversion was only 18.0%. The syngas feed rate was then increased by 50%, but the CO conversion increased only 21.6%. It was decided to end the run at this time and repeat it in the near future.

Run No. 21 in the M4-SBCR was started on September 19th with Catalyst No. Co.004. This catalyst is similar to Catalyst No. Co.002 used in Run 3, M4-SBCR, but was not calcined before hydrogen reduction. The CO conversion was much higher than with the calcined version of this catalyst, 39.3% vs. 29.4%. The CO conversion stayed higher over the entire run and remained higher after 227 hours on stream than with the calcined catalyst, 34.6% vs. 24.2%. The methane selectivity, however, was high, averaging about 16% for both the calcined and uncalcined versions of this catalyst.

Data for Runs 5 to 29 in M3-SBCR and Runs 3 to 21 in M4-SBCR are compiled on Tables I through X found in Appendix C.

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 5 to 29 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 are used to present the comparison of catalyst activities for Runs 3 to 21 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX and X in Appendix C).

(2) Discussion of Results

One test run was made in the M4-SBCR (see Run 14 in Table 6 in which 15.0 gm of Catalyst No. Co. 005 plus 5.0 gm of Catalyst No. WGS.03 were charged as a blend. This was a test run in which a cobalt-alumina based catalyst for methane reduction was mixed with a water gas shift catalyst. The CO conversion was slightly higher than using only Catalyst No. Co.005, 29.3% vs 27.1%. The CH_4 selectivity was slightly higher, 10.1% vs. 7.9%, but the CO_2 selectivity increased from 0.8% to 2.0%, an insignificant amount. A run will be made in the near future in which equal amounts of the same two catalysts will be charged.

One run was made to evaluate the addition of zirconium on an alumina supported catalyst. The CO conversion was similar to that obtained with alumina catalyst with no additives (see Run 15 in Table 6), but the CH_4 selectivity was slightly higher, 10.4% vs. 7.9%. Adding

a high concentration of Zr to the cobalt-alumina based catalyst did not increase the CO conversion nor lower the CH_4 selectivity.

Five samples of catalysts were received from Calsicat to test in the SBCR. Each was prepared to match the Catalyst No. Co. 047 prepared by Pitt: 20 wt% Co, 0.5% wt% Ru, and 0.3 wt% K on gamma-alumina support. Two samples, CAL.04 and CAL.05, were calcined in air and nitrogen, respectively. The third sample, CAL.06, was hydrogen reduced and air stabilized. The last two samples, CAL.07 and CAL.08, are reduced powder immersed in paraffin wax and crushed into granules. CAL.08 was calcined in nitrogen before reduction while CAL.07 was processed with hydrogen during the entire heat treatment.

Catalyst No. CAL.04 yielded a CO conversion that was about 2% lower than the same catalyst Co.047, which was prepared by Pitt (see Runs 16-M4 and 23-M3 in Table 7). The CO conversion and CH_4 selectivity for Catalyst No. CAL.05 were nearly identical, (see Runs 16-M4 and 19-M4 in Table 7). Calcining the catalyst in nitrogen instead of air showed no beneficial effect.

Catalyst No. CAL.08 which had been encapsulated in wax yielded only 16.9% CO conversion with a 5.9% CH_4 selectivity (see Run 17-M4 in Table 7). The second wax encapsulated catalyst, CAL.07, produced a slightly higher CO conversion, 20.6%, with a corresponding increase of CH_4 selectivity to 7.7% (see Run 18-M in Table 7). The loss of catalyst activity may have been due to air diffusing through the wax coating during storage or while handling and charging the catalyst slurry into the reactor. Another was encapsulated catalyst has been received from Calsicat and will be tested in the near future.

The fifth sample from Calsicat, CAL.06, had been hydrogen reduced and then stabilized with air. The purpose was to see how much residual activity the catalyst would have even though it had been oxidized. The CO conversion was 5.6% at startup conditions and demonstrates that a reduced catalyst that had been stabilized with air has some residual activity (see Run 20-M4 in Table 7).

A larger amount of catalyst, 25.2 gm was charged to M3-SBCR to study catalyst loading and to obtain higher syngas conversion levels. A summary of the CO conversion, production rates, and production selectivities are given in Table 8.

The initial CO conversion was higher due to the larger amount of catalyst charged. CH_4 selectivity was high since this catalyst had no potassium to reduce the CH_4 rate. The CO conversion and production rates and selectivities were typical for this catalyst but at a higher level because of the larger amount of catalyst.

For Period 7, the syngas feed rate was reduced in half with a corresponding increase in nitrogen feed. The CO conversion dropped from 40.8% to 31.5% mainly because of the reduction in the syngas partical pressure. Raising the temperature to 260°C did not change the CO conversion (see Period 8). At this point, it was suspected that the catalyst had been partially deactivated. The reactor was then returned to startup conditions, but the CO conversion was only 18%, see period 9 on Table 8. One last period was made in which the syngas feed rate was increased to 150% of normal flows, but the CO conversion only increased to 21.6%. It is not known at this time why the CO conversion dropped. It is possible that the lead oxide beads

were saturated and lost their ability to remove iron carbonyls from the CO feed gas. This run will be repeated in the near future.

Catalyst No. Co.004 was charged to M4-SBCR but was not calcined before hydrogen reduction. This catalyst was identical to Catalyst No. Co.002 which was calcined. The CO conversion was much higher than the calcined version, 39.3% vs. 29.4% (see Runs 3 and 21 in M4-SBCR in Table 6). The CO conversion stayed higher over the entire run (227 hours). CO conversion of uncalcined catalysts has been observed to decrease faster in the fixed bed reactor studies. The methane selectivity, however, was high, about 16%, for both versions of this catalyst.

In conclusion, several catalysts supplied by Calsicat have been tested in the SBCR's and two samples have produced similar results to those formulated by Pitt. The wax coated catalysts, however, showed lower catalyst activity. Additional samples supplied by Calsicat will be tested as soon as they are received. Adding Zr to the Co-alumina based catalyst had no beneficial effect on lowering CH_4 production. Mixing two catalysts, 1/4 water gas shift catalyst + 3/4 cobalt catalyst, produced only a small amount of water gas shift activity. Running with a catalyst that was uncalcined before hydrogen reduction yielded about a 30% increase in catalyst activity. Finally, the high CO conversion hydrogen reduction yielded about a 30% increase in catalyst activity. Finally, the high CO conversion test run yielded a maximum of only 42% CO conversion. This run will be repeated in the near future.

(3) Catalyst Recovery Analyses

The catalysts charged for all runs, except for Run 20 in M3 and for Run 2 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 9. 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 9. 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 9.

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 M4-SBCR in Table 9).

Five 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 9). 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.

VII. 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 on both reactor systems.

A selected number of catalysts will be tested at high pressure (similar to the conditions used in the slurry bubble column reactor) for direct comparison with the SBCR data.

The fixed-bed reactor testing of the series of Al_2O_3-supported Co catalysts with a water-gas shift function 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);
- Temperature programmed desorption (TPD).

C. New catalyst formulations will be generated in order to pursue the effect of selectivity promoters. The formulation of new Co F-T catalysts having water-gas shift activity will be continued using different preparation techniques for the incorporation of Co into the most active Al_2O_3-supported WGS catalysts.

D. The investigation of the effect of pretreatment conditions including calcination and reduction will be continued.

E. In the slurry bubble column we shall:

1. Attempt several high conversion runs with high activity catalyts.

2. Test Calsicat produced catalysts as they are received.

3. Install a chilled water pre-cooling coil in the feed gas line to one of the SBCRs before another high CO compression run is attempted.

4. A new bunch of Catalyst No. Co.053 will be chabed to determine the effect of catalyst loading and to obtain high CO conversion levels.

5. A blend of Catalyst No. Co.005 and Catalyst No. WGS.09 will be charged for Run 22 in M4-SBCR to evaluate the water gas shift reaction with 3 times the amount of water gas shift catalyst.

6. Calsicat will produce a catalyst similar to our Catalyst No. Co.047 which contains 20 wt % Co, 0.5 wt % Ru, and 0.3 wt % K on gamma-alumina. This catalyst will be tested in both the fixed bed reactor and the SBCR.

VIII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

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