2

Key D

AU-3
3

AUG 12 1993

TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

Contract No. DE-AC22-92PC92108

QUARTERLY TECHNICAL PROGRESS REPORT NO. 2

Covering the Period January 1, 1993 to March 31, 1993

Prepared for
U.S. Department of Energy
Pittsburgh Energy Technology Center
PETC Project Manager: Arun Bose
P. O. Box 10940
Pittsburgh, PA 15236

Submitted by:
Principal Investigator - Dr. Alan H. Singleton
Energy International Corporation
135 William Pitt Way
Pittsburgh, PA 15238

April 29, 1993
Final Issue Date: July 27, 1993

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

Se

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page No.</u>
I. INTRODUCTION AND BACKGROUND	1
II. PROJECT DESCRIPTION	1
III. OBJECTIVES	2
IV. PLANS FOR THIS QUARTER	3
V. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER	3
VI. DETAILED DESCRIPTION OF TECHNICAL PROGRESS	4
A. Task 1: Catalyst Development	4
1. Technology Assessment	4
2. Catalyst Formulation	4
3. Catalyst Characterization	5
B. Task 2: Catalyst Testing	6
VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS	10
VIII. REFERENCES	10
IX. APPENDIX	A-1

ACKNOWLEDGEMENTS

The following persons contributed to this report: George Haddad, Andreas Kogelbauer, Rachid Oukaci, James G. Goodwin, Jr. and George Marcelin, all from the University of Pittsburgh; William Gall, Ronald W. Genser, and Alan H. Singleton, all from Energy International Corporation.

LIST OF TABLES

	<u>Page No.</u>
Table 1 - List of Catalysts Formulated	11
Table 2 - Chemical Elemental Analysis	12
Table 3 - Supports Elemental Analyses	13
Table 4 - Summary of Support Properties	14
Table 5 - Cobalt Catalyst Characteristics Determined by H ₂ Chemisorption and XRD	15
Table 6 - Performance of Co.000 Catalyst for F-T Synthesis	16
Table 7 - Performance of Co.001 Catalyst for F-T Synthesis	17

LIST OF FIGURES

Figure 1 - Silica Particle Size Distribution	18
Figure 2 - Silica Pore Size Distribution	19
Figure 3 - Silica Pore Size Distribution	20
Figure 4 - Alumina Pore Size Distribution	21
Figure 5 - Alumina Pore Size Distribution	22
Figure 6 - XRD Pattern for Catalyst Co.000	23
Figure 7 - XRD Pattern for Catalyst Co.001	24
Figure 8 - XRD Pattern for Catalyst Co.002	25
Figure 9 - XRD Pattern for Catalyst Co.009	26
Figure 10 - Static H ₂ Chemisorption at 100°C, Catalyst Co.000	27
Figure 11 - Static H ₂ Chemisorption at 100°C, Catalyst Co.009	28
Figure 12 - Schematic of the Fixed-Bed Reactor System	29
Figure 13 - Arrhenius Plot for Co.000 - 30% Co/0.45% K/0.245% Ru/Al ₂ O ₃	30

LIST OF FIGURES
(Continued)

	<u>Page No.</u>
Figure 14 - Schulz-Flory Distribution on Co.000 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=11 hrs, CO Conv.=5.96%	31
Figure 15 - Schulz-Flory Distribution on Co.000 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=25 hrs, CO Conv.=8.10%	32
Figure 16 - Schulz-Flory Distribution on Co.000 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=55 hrs, CO Conv.=4.70%	33
Figure 17 - Schulz-Flory Distribution on Co.000 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=220°C, t=80 hrs, CO Conv.=9.70%	34
Figure 18 - Schulz-Flory Distribution on Co.000 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=92 hrs, CO Conv.=5.30%	35
Figure 19 - Schulz-Flory Distribution on Co.001 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=24 hrs, CO Conv.=2.60%	36
Figure 20 - Schulz-Flory Distribution on Co.001 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=48 hrs, CO Conv.=2.62%	37
Figure 21 - Schulz-Flory Distribution on Co.001 - Conditions: wt=0.1 g, F=50 cc/min, P=1 atm, H ₂ :CO=2, T=210°C, t=72 hrs, CO Conv.=2.52%	38
Figure 22 - Slurry Bubble Column Reactor - Catalyst Test Unit	39

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. PLANS FOR THIS QUARTER

TASK 1.0 - Catalyst Development

This task focuses on the identification of catalyst compositions, development of preparation methods, and catalyst characterization followed by or in conjunction with initial catalyst screening (see Task 2.1 - Fixed Bed Testing) with the goal of producing an optimized Co F-T catalyst with low methane selectivity and enhanced WGS activity. Within this task, a number of activities are planned to be carried out at the University of Pittsburgh.

(a) Technology Assessment (Subtask 1.1) - The objective of this task is to evaluate all the pertinent open and patent literature on Co F-T catalysts in order to ascertain the current status of Co-based catalyst technology for F-T synthesis.

(b) Catalyst Formulations (Subtasks 1.2-1.4) - Based on the technology assessment and the team's experience, catalyst formulations will be developed focusing essentially on meeting the performance criteria established for this task.

(c) Catalyst Characterization (Subtask 1.6) - A number of physical and chemical characterization techniques will be used in order to gain a better understanding of the Co F-T catalyst properties.

TASK 2.0 - Catalyst Testing

The objective of this task is to determine those catalyst formulations which meet the desired performance criteria. Initial catalyst testing will be carried out in a small-scale fixed-bed reactor followed by slurry bubble column reactor testing of those catalysts which exhibit satisfactory performance in the fixed-bed tests. The initial screening of catalyst performance in fixed-bed reactors (Subtask 2.1) will be carried out at the University of Pittsburgh; and subsequent testing in the slurry bubble column reactor system (Subtask 2.2) will be carried out at Energy International. Refurbishment and refitting of the slurry bubble column reactor units as well as commissioning were planned for this reporting period, which consisted of procurements and installation and a "shakedown" run.

V. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

A second computer search of the patent literature was conducted. Review and evaluation of both the open and patent literature continued during this reporting period (Task 1).

Another series of benchmark and base catalysts based on the patent literature was established, and their formulations were developed. Nine catalysts (of those twelve which have been formulated) were prepared during this reporting period (Task 1).

Elemental analyses of all the chemicals and supports acquired for catalyst preparation were carried out in order to determine the level of impurities, if any. The physical properties of the supports (i.e. BET surface area, pore volume, pore size distribution, and particle size distribution) have been determined. Cobalt dispersion was determined for some of the catalysts by both static H₂ chemisorption and XRD (Task 1).

Fixed bed testing of the catalysts was started during this reporting period. However, the initial runs of the fixed bed reactor with one of the benchmark catalysts revealed a number of problems with the on-line analysis of the F-T products. Further modifications of the sampling system were carried out in order to improve the reaction system (Task 2).

New reactors, flow meters, a gas chromatograph, a data acquisition system, and various peripherals were installed on the two slurry bubble column reactor units located at Energy International. A "shakedown" run was made late this quarter in anticipation of the April 1st start of the experimental program (Task 2).

VI. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. TASK 1 - Catalyst Development

1. Technology Assessment (Subtask 1.1)

Copies of patents ordered early in this reporting period were received late in February; review and evaluation of the patent literature are underway. Likewise, because of the huge number of references to be evaluated, review and evaluation of the non-patent literature is still underway.

A second computer search of the patent literature was conducted during this reporting period. This search was restricted to patents of the major patent assignees in the area of Co F-T catalysis. About 30 patents which did not appear in the previous computer search were assigned to the first 5 patent assignees listed in Table 1 in the previous quarterly report. Copies of the missing patents were also ordered but not yet received.

The delay in the reception of copies of the patents that have been ordered as well as the significant number of publications that have to be analyzed extend the technology assessment task into the next reporting period. However, this should not affect in any way the plans for achieving the contract objectives.

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

Another series of benchmark catalysts has been established based on patents from Shell and Exxon, the two other major players in Co F-T catalysis. In addition, a series of base unpromoted Co catalysts on the same supports used for the various patented catalysts have been formulated. The complete list of the benchmark and base catalysts formulated so far (including those catalysts listed in the previous quarterly report) is given in Table 1 with their composition. The last column of Table 1 indicates whether the catalyst has already been prepared. The detailed formulations of the new catalysts are given in the appendix. Although all of these

catalysts are prepared following the procedure given in the corresponding patents, a small batch of each of the catalyst is retrieved before calcination. These non-calcined catalysts will be used to investigate the effect of calcination temperature on their catalytic properties.

3. Catalyst Characterization (Subtask 1.6)

Chemicals Elemental Analysis

Elemental analyses of all the chemicals acquired for catalyst preparation were carried out in order to determine the concentration of known and possible impurities which may be contained in these chemicals. The results are shown in Table 2. The concentrations of all the elements listed in Table 2 were determined by ICP at PARC. The results show that all the chemicals used in catalyst preparation were relatively pure, except for $\text{RuNO}(\text{NO}_3)_2$ which contained more than 7% by weight of sodium. An independent analysis of $\text{RuNO}(\text{NO}_3)_2$ at Galbraith Laboratories found a similar result. The high concentration of Na in $\text{RuNO}(\text{NO}_3)_2$ was attributed to the process used for the production of this compound in which the manufacturer uses a sodium salt in the crystallization step followed by an inefficient washing step.

This sodium contamination is not believed to produce more than second order effects in catalyst performance due to the overpowering effects of the deliberate addition of either potassium or rare earths in all of those formulations in which the ruthenium is used.

Similar elemental analyses were carried out on the supports (alumina and silica). The results are listed in Table 3. The Vista B alumina was relatively pure, containing less than 0.01% of all the elements analyzed for. Silica contains higher concentrations of some of the elements (Mg, Na, Ca, Ti, Al, K, S). However, these levels of impurities are below the limits which are known to affect catalyst properties and performance.

Support Physical Properties

The particle size distribution of the supports were measured using a MicroTrac particle size analyzer. The supports were sieved to a 0-400 mesh prior to the particle size analysis in order to eliminate particle size ranges unsuitable for slurry bubble column operation. The distribution obtained for silica is shown in Figure 1.

Nitrogen physisorption at 77 K was used to obtain surface area and pore size distribution of the supports. Pore size distributions based on both pore area and pore volume are plotted in Figures 2-3 and 4-5 for silica and alumina respectively. Table 4 gives a summary of the support physical properties.

XRD Measurements

X-ray diffraction measurements were performed on a Philips X'pert System XRD machine with monochromatized Cu K_α radiation. The XRD instrument was operated at 40 kv and 30 mA. The catalyst powders were supported on a

glass slide for measurement. The spectra were scanned at the rate of 2.4 deg/min (in 2θ). The XRD patterns for some of the catalysts are shown in Figures 6-9. A summary of the results is given in Table 5.

Static Hydrogen Chemisorption

The gas volumetric chemisorption was determined according to the method of Reuel and Bartholomew.¹ Prior to chemisorption measurements, all the catalysts were pre-reduced in a flow system and passivated before storage. Static hydrogen re-reduction of the catalyst was performed at 320°C for 15 hours. This temperature was chosen so that it would be lower than the 350°C reduction temperature to minimize any further catalyst modifications that could be induced if higher temperatures were used. After H₂ chemisorption at 100°C for 5 hours the adsorption isotherms were measured at 25°C by the decreasing pressure method. The high temperature for adsorption was used since the cobalt adsorption process is known to be an activated process.¹ One hour was allowed for equilibrium at each H₂ pressure. The total adsorption isotherm was obtained. The reversible H₂ desorption isotherm was measured following evacuation of the catalyst for 10 minutes at 25°C. The total and reversible amounts of H₂ adsorbed were obtained by extrapolating the isotherms to zero pressure. The number of total chemisorbed H atoms was used to determine the number of vacant Co atoms at the surface by using the relation $H_{TOT}/Co_S=1$ determined by Reuel and Bartholomew.¹

Static H₂ chemisorption isotherms are plotted in Figures 10-11. Table 5 summarizes the properties of some of the catalysts as determined by H₂ chemisorption and XRD measurements.

B. TASK 2.0 - Catalyst Testing

1. Fixed Bed Reaction System

The original setup of the reaction system (see Figure 12) included the following components:

- gas supply controlled by mass flow meters
- 6-port valve to alternately feed reactants or bracketing gas
- reactor and oven (temperature-controlled)
- pressure control and measurement
- Cold trap before the back pressure regulator to prevent condensation of products in the back pressure regulator
- leak valve at the reactor outlet to divert part of the product stream to the GC
- 6-port sampling valves with sample loops for the GC, carrier gas supply through the GC
- FID equipped with a DB-1 Megabore column for heavy hydrocarbon separation and detection, TCD equipped with a 6' Porapak Q for separation and detection of CO, H₂, CO₂ and C₁ to C₆ hydrocarbons.

The initial runs of the fixed-bed reactor with one of the benchmark catalysts revealed a number of problems with the on-line analysis of the F-T products. Some modifications on the reactor system have been carried out in order to improve the product analysis. A temperature-controlled trap was installed between the GC sampling valves and the needle valve that restricts the flow to these valves. By keeping the temperature of this trap somewhat lower than the rest of the system (around 200°C), the heaviest hydrocarbons are now condensed before they reach the sampling valves and subsequently the columns. In order to further reduce any accumulation of heavy hydrocarbons in the lines going to the GC a heated 6-port valve was installed upstream of the needle valve. This arrangement enables a continuous purging of the lines going to the GC with helium. The products are allowed to flow through the lines and the GC sampling valves for only a short time (usually 10 minutes) before taking the sample. This setup has been installed and was being tested successfully at the end of this reporting period.

In addition, another capillary column (30M, 0.32mm DB-5) was tested, allowing faster elution of the heavy ends, thus, reducing the danger of product accumulation on the column. The 6' Porapak column was also replaced with a 12' column in order to improve separation of the light hydrocarbons and the inert gases. The disadvantage lies in the incompatibility of the capillary column with the packed column, a 12 feet 1/8" Porapak Q in terms of maximum temperature (250°C for the Porapak Q vs. 320°C for the capillary column). The analysis of the permanent gases and the low molecular weight hydrocarbons may have to be carried out in a separate GC if higher than 250°C temperatures are required for good performance of the capillary column.

Experimental

The procedures described in this section have been used for the initial test runs before any of the modifications described above have been implemented.

(a) Pretreatment

The catalyst was held in place in a U-shaped stainless reactor using glass wool. The calcined catalyst was heated from room temperature to 350°C at 1°C/min in 50 cc/min flowing hydrogen. It was then reduced in hydrogen at 350°C for 10 hours to avoid cobalt aluminate formation. The hydrogen used was ultrapure (Linde) with further purification using a deoxo unit followed by a molecular sieve trap. The reduced catalyst was cooled down to the reaction temperature of 210°C in 50 cc/min of flowing hydrogen. Flow rates were controlled by Brooks flow controllers and the temperatures were controlled by Omega temperature controllers.

(b) Reaction Studies

The reaction conditions were selected to give differential reaction conversion levels. In order to start the reaction, the flow was switched to 33.3 cc/min H₂ and 16.67 cc/min CO (H₂:CO = 2, total flow = 50 cc/min). The reaction was carried out at ambient pressure in the differential fixed bed reactor. Reaction was continued at 210°C for 25 hours when

steady state was reached. The temperature was gradually decreased to 200, 190, and the reaction was carried out at these temperatures to obtain an Arrhenius plot. The temperature was increased back to 210°C at 1°C/min to check for possible deactivation.

The post reactor zone was heated at 300°C to avoid condensation of waxes. A glass U-tube trap at room temperature was used to collect the condensable products before the vent line (but after the GC injection valve). Product gases were passed to a Perkin Elmer gas chromatograph for on-line analysis. The GC was equipped with a 30 meter DB-1 Megabore capillary column and FID. The GC oven was held at 35°C for 2 min. It was then heated to 200°C at 5°C/min and held there until the analysis was complete. Ultra-pure helium (Linde) passed through a molecular sieve trap was used as a carrier gas for FID, at a flow rate of 5 cc/min. For this run a Varian 3700 GC equipped with Porapak 80/100 column of 6 ft length was used to do manual injection of samples and then relate the C₄ signal back to the Perkin Elmer chromatograph. The two chromatographs were calibrated using pure hydrocarbons to determine retention times, amounts, and types of the products.

(c) Treatment of Data

The rates of product formation were calculated using the following formula:

$$R = XF/W$$

where R is the rate, X is the fractional conversion, F is the reactant flow rate, and W is the catalyst loading. Product GC areas were used to obtain the Schulz-Flory distribution. Chain growth probability (α) was obtained by fitting a straight line to the data for C₄ to C₁₁ products in a S-F plot. It has been accepted in the scientific literature² that such procedure gives an accurate prediction of α . C₁₂-C₂₀ fell slightly above the S-F distribution predicted by α . Such a problem can arise due to the condensation of heavier hydrocarbons in the sampling loop.

(d) Results

Two catalysts were tested during this reporting period. One catalyst, not listed in Table 1, termed Co.000 and developed in a previous study was used as an in-house standard to evaluate the performance of the reactor system. The second catalyst tested was Co.001. Few reliable results were obtained with the latter before a number of analytical problems occurred due to heavy hydrocarbon condensation in the lines.

The performances of catalysts Co.000 and Co.001 are given in Tables 6 and 7, respectively. Because of the difficulties encountered in analyzing the heavy hydrocarbons (>C₁₅), a limited product distribution from C₁ to C₁₅ as obtained by GC analysis is given first in the Tables as a function of time-on-stream and temperature. The chain growth probability, α , is determined using C₄-C₁₂ hydrocarbon products. The estimated total product distribution (up to C₂₀) was obtained using the values of α to determine the concentrations of C₁₃-C₂₀. Finally, the percent CO conversion determined from the estimated product distribution and the rate of hydrocarbon production in g CH₂/g catalyst/h are also given in Tables 6 and 7.

The Arrhenius plot and the Schulz-Flory distribution plots for Co.000 are shown in Figures 13-18. The overall performance of Co.000 was in agreement with results obtained previously using this same catalyst.

Because of the problems of condensation and accumulation of heavy products mentioned in the previous sections, only a limited number of reliable GC analyses were obtained for Co.001. These results are shown in Table 7. The corresponding Schulz-Flory distribution plots are given in Figures 19-21. From the limited reliable data obtained, the performance of this catalyst was found to be in agreement with the results reported for a similar catalyst.³ The performance of the catalyst Co.001 will be re-evaluated once all the analytical problems are solved with the new sampling system setup.

2. Slurry Bubble Column Reaction System

During this reporting period procurements and installations were made for the purpose of refurbishing and refitting the two SBCR units that had been used in the recent past for Fischer-Tropsch development projects. The objective of Subtask 2.2 is to test in a slurry bubble column reactor catalysts that have shown satisfactory performance in a fixed-bed reactor. This is necessary because catalysts which perform satisfactorily in a fixed bed environment will not necessarily perform as well in a slurry environment. Catalyst density is particularly important. A catalyst with a high metals loading may show high activity in a fixed bed but perform poorly in a slurry reactor due to catalyst settling.

Successful development of new or improved catalysts requires catalyst testing at various levels. Because complete testing (aging, complete characterization, etc.) of a catalyst is very expensive and time consuming, such complete testing will only be done for a select number of samples. Thus, it is imperative that preliminary testing be conducted in a rapid and efficient manner to reduce the number of catalyst formulations that proceed to further testing.

Two virtually identical units, called M-3 and M-4, have been created from existing equipment/hardware with the addition of new procurements. Also, design modifications were made as a result of experience with operation of the units under related and similar conditions. Two reactors, four mass flow meters, two tanks and associated piping, wiring, instrumentation and insulation have been added to the units. A gas chromatograph and a data acquisition system will serve both units. The PC-based data logger will collect and retain raw data for data usage in real time for operations and for data reduction for reporting.

Figure 22 presents a schematic flow diagram of the SBCR units described above. The reactors are 1-inch ID x 36 inches long tubes. Proprietary technology is employed for separation of the heavy product from the catalyst. Up to 15 grams of pretreated catalyst are charged batchwise into a reactor using a carrier liquid (usually synfluid, a Chevron produced polyalphaolefin in the C₃₀ to C₅₀ range, which is used as the initial catalyst vehicle). Syngas is fed continuously to the reactor, and provision has been made to add additional liquids, such as synfluid, water, and recycled oil. The gaseous products leave the top of the reactor and go to a system of product traps, gas meters, and analyzers. Excess heavy product

continually drains from the reactor. The off-gas is periodically analyzed by a gas chromatograph, and conversion and selectivities of the light hydrocarbons are calculated. Samples of the collected water and hydrocarbon products can be submitted for various analyses.

The following parameters can be varied: reaction temperature, reaction pressure, syngas composition, syngas feed rate (superficial gas velocity), and the feed rates of extraneous liquids, such as water, synfluid, and recycle product. (It is unlikely that any of these materials would be added into this work.) Mass balances based on carbon, hydrogen and oxygen balance, catalyst activity, product selectivities, and catalyst aging data can be calculated using an on-line data collection system.

Each catalyst test run will require a minimum of five consecutive days of operation. Only catalyst formulations passing the fixed-bed screening will be tested.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

As noted in the previous report, Subtask 1.1 (Technology Assessment) is running behind schedule because of the huge number of references to be surveyed and the subsequent time-consuming process of reviewing/evaluating the publications. Despite this delay, the contract objectives should not be affected adversely. The technical approach which has been proposed remains the same and all the other tasks are proceeding within schedule.

VIII. REFERENCES

1. Reuel, R.C., and Bartholomew, C.H., J. Catal. 85, 63 (1984).
2. R. Snel, J. Zwart, Appl. Catal. 22, 337 (1986).
3. Eri, S., Goodwin, J.G., Jr., Marcelin, G. and Riis, T., U.S. Pat. 4,880,763 (1989).

Table 1. List of Catalysts Formulated

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.001	20%	1% Re	1% La ₂ O ₃ 0.13% K	γ-alumina	U.S. Pat. 4,880,763	P
Co.002	20%	0.43% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	P
Co.003	20%	0.5% Ru	1% La ₂ O ₃	γ-alumina	U.S. Pat. 4,413,064	-
Co.005	20%	0	0	γ-alumina	Base Catalyst	P
Co.006	20%	0.75% Re	0	Titania	U.S. Pat. 4,794,009	-
Co.007	20%	0	0	Titania	Base Catalyst	-
Co.008	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A	P
Co.010	20%	0	0	γ-alumina	Base Catalyst (non-calcined)	P
Co.011	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A	P
Co.012	20%	0	0	Silica	Base Catalyst (Inc. Wetness)	P

Table 2. Chemicals Elemental Analyses

	Weight %									
	KNO ₃	Co(NO ₃) ₂	RuNO (NO ₃) ₂	H ₂ PtCl ₆	La(NO ₃) ₃	HReO ₄	ZrO (NO ₃) ₂	Co(NO ₃) ₂ Lot A11G	RuAcAc	RuNO (NO ₃) ₂
Cu	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Co	<.01	-	<.01	<.01	<.01	<.01	<.01	-	<.01	<.01
Mg	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Na	<.01	<.01	6.3	<.01	<.01	<.01	0.10	<.01	<.01	7.4
Ba	<.01	<.01	<.01	<.01	<.01	<.01	0.01	<.01	<.01	<.01
Mn	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Ca	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Zn	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Ti	<.01	<.01	<.01	<.01	<.01	<.01	0.04	<.01	<.01	<.01
Cr	<.01	<.01	<.01	<.01	<.01	<.01	0.01	<.01	<.01	<.01
Al	0.02	<.01	<.01	<.01	<.01	<.01	0.46	<.01	<.01	<.01
Pb	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Fe	<.01	<.01	<.01	<.01	<.01	<.01	0.05	<.01	<.01	<.01
Mo	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
As	<.01	<.01	0.03	<.01	<.01	<.01	<.01	<.01	0.03	0.03
Ni	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Sb	<.01	<.01	0.01	<.01	<.01	<.01	<.01	<.01	0.01	0.01
Sr	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
V	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
P	<.01	<.01	<.01	0.07	<.01	<.01	0.18	<.01	<.01	<.01
Ce	<.01	<.01	<.01	<.01	0.02	<.01	<.01	<.01	<.01	<.01
La	<.01	<.01	<.01	<.01	-	<.01	<.01	<.01	<.01	<.01
K	-	<.01	0.07	<.01	<.01	<.01	<.01	<.01	<.01	<.01
S	<.01	<.01	<.01	<.01	<.01	<.01	0.05	<.01	<.01	<.01

Table 3. Supports Elemental Analyses

	Silica 952, ppm	Alumina, Vista-B, wt %
Cu	<10	<.01
Co	<10	<.01
Mg	150	<.01
Na	570	<.01
Ba	<10	<.01
Mn	<10	<.01
Ca	750	<.01
Zn	<10	<.01
Ti	120	<.01
Cr	<10	<.01
Al	220	-
Pb	<10	<.01
Fe	96	<.01
Mo	<10	<.01
As	<10	<.01
Ni	<10	<.01
Sb	<10	<.01
Sn	<10	<.01
V	<10	<.01
P	83	<.01
Ce	<10	<.01
La	<10	<.01
K	160	<.01
S	30	<.01

Table 4. Summary of Support Properties

	Silica 952	Alumina, Vista-B
BET Surface Area, m ² /g	299	219
Pore Volume, cc/g	1.69	0.51
Average Pore Diameter (vol.), Å	269	89
Average Pore Diameter (area), Å	204	70
Median Pore Diameter (vol.), Å	373	95
Median Pore Diameter (area), Å	270	58
Median Particle Size (0-400 mesh), μm	115	

Table 5. Co Catalyst Characteristics determined by H₂ Chemisorption and XRD

Catalyst	H ₂ Chemis. ^a (μ mol H/g cat)		Avg. dp ^b (nm) by Chemis.	% Dispersion	Crystal Phases by XRD	Avg. dp (nm) by XRD
	total	irrev				
<u>Co.000</u>	75	70	34	3	Co ₃ O ₄ γ -Al ₂ O ₃	36
<u>Co.009</u> 30%Co, 0.45%K, 0.245%Ru	134	125	19	5.3	Co ₃ O ₄ γ -Al ₂ O ₃	22
<u>Co.001</u> 20%Co, 0.13%K, 1.34%Re, 1%La ₂ O ₃					Co ₃ O ₃ γ -Al ₂ O ₃	26
<u>Co.002</u> 20%Co, 0.43%Ru, 1%La ₂ O ₃					Co ₃ O ₄ γ -Al ₂ O ₃	19

(a) Static H₂ Chemisorption at 100°C.

(b) Est. assuming $H_{\text{ox}}/\text{Co}_\text{s}=1$, 5.46×10^{-20} m²/Co, and $dp=5/S_{\text{Co}}/\rho$

Table 6 Performance of CO.000 catalyst for FT synthesis

Catalyst : CO.000, Pressure = 1 atm, Flow rate = 50 cc/min, Catalyst loading=0.1 g
 H₂/CO ratio in feed =2

Time on stream, hr Reaction temperature, C	11 210	25 210	55 210	80 220	84 190	88 200	92 210
C1-C15 Product distribution, weight %							
C1	13.1	14.4	17.5	22.5	8.2	10.3	16.1
C2	2.2	2.5	3.1	3.8	1.8	2.0	2.8
C3	5.2	5.8	7.2	9.0	3.3	4.3	6.4
C4	10.0	7.0	7.8	10.0	5.0	6.7	7.6
C5	5.6	6.3	7.6	8.6	5.3	6.6	6.5
C6	9.4	5.8	6.4	5.8	3.4	3.5	5.2
C7	6.9	5.8	7.0	6.9	7.2	6.5	7.1
C8	5.8	5.8	6.0	6.0	5.3	6.4	8.8
C9	6.6	8.1	5.6	4.7	5.4	7.2	5.3
C10	4.0	5.7	5.7	4.4	5.8	7.0	6.3
C11	4.8	7.0	5.9	3.7	7.0	9.9	5.9
C12	7.4	6.9	5.0	3.8	8.0	9.2	6.1
C13	9.6	6.9	5.2	3.3	9.2	8.4	6.4
C14	5.6	5.9	5.1	4.4	11.2	11.9	6.0
C15	4.0	6.3	4.9	2.9	14.0	*	6.8
alpha chain growth probability	0.87	0.89	0.83	0.78	0.9*	0.93*	0.85
Estimated total product distribution, weight %							
C1	12.	11.	16.	22.	7.	5.	15.
C2+C3	7.	6.	9.	12.	5.	3.	8.
C4-C11	48.	38.	47.	43.	39.	28.	45.
C12-C20	33.	46.	27.	18.	49.	63.	32.
CO conversion, %	5.96	8.10	4.70	9.70	1.70	4.70	5.30
Rate, g CH ₂ /g cat/hr	0.37	0.51	0.29	0.60	0.10	0.30	0.33

* data not reliable

Table 7 Performance of CO.001 catalyst for FT synthesis

Catalyst : CO.001, Pressure = 1 atm, Flow rate = 50 cc/min, Catalyst loading=0.1 g
 H₂/CO ratio in feed =2

Time on stream, hr	24	48	72
Reaction temperature, C	220	220	220
C1-C15 Product distribution, weight %			
C1	26.6	30.3	27.9
C2	4.9	5.5	5.1
C3	11.8	12.3	11.6
C4	11.9	12.1	11.6
C5	10.8	9.9	9.4
C6	5.6	8.6	7.0
C7	6.0	7.8	13.0
C8	5.7	3.8	3.5
C9	3.3	2.6	2.6
C10	5.0	1.9	1.9
C11	2.4	1.6	1.8
C12	1.7	1.1	1.3
C13	1.3	0.8	0.9
C14	0.9	0.6	0.7
C15	0.7	0.4	0.5
alpha chain growth probability	0.65	0.66	0.68
Estimated total product distribution, weight %			
C1	27.	30.	28.
C2+C3	17.	18.	17.
C4-C11	51.	48.	51.
C12-C20	5.	4.	4.
CO conversion, %	2.60	2.62	2.52
Rate, g CH ₂ /g cat/hr	0.16	0.16	0.16

* data not reliable

```

;MMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMM9
  Esc-exit          F2-commands          :

```

Figure 2. Silica Pore Size Distribution

Figure 3. Silica Pore Size Distribution

Figure 4. Alumina Pore Size Distribution

Figure 5. Alumina Pore Size Distribution

Fig. 6 XRD Pattern for Catalyst Co.000

Fig. 7 **XRD Pattern for Catalyst Co.001**

Fig. 8 **XRD Pattern for Catalyst Co.002**

Fig. 9 XRD Pattern for Catalyst Co.009

Figure 10 Static H₂ Chemisorption at 100 °C, Catalyst Co.000

Figure 11 Static H₂ Chemisorption at 100 °C, Catalyst Co.009

Fig. 12 Schematics of the Fixed Bed Reactor System

Fig. 13 Arrhenius Plot for Co.000
30% Co/0.45%K/0.245%Ru/ Al_2O_3

Fig. 14 Schulz-Flory Distribution on Co.000
Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
H₂:CO=2, T=210° C, t=11 hrs, CO Conv.=5.96%

Fig. 15 Schulz-Flory Distribution on Co.000
 Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
 $H_2:CO=2$, T=210°C, t=25 hrs, CO Conv.=8.10%

Fig. 16 Schulz-Flory Distribution on Co.000
 Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
 $H_2:CO=2$, T=210°C, t=55 hrs, CO Conv.=4.70%

Fig. 17 Schulz-Flory Distribution on Co.000
Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
H₂:CO=2, T=220°C, t=80 hrs, CO Conv.=9.70%

Fig. 18 Schulz-Flory Distribution on Co.000
 Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
 $H_2:CO=2$, T=210° C, t=92 hrs, CO Conv.=5.30%

Fig. 19 Schulz-Flory Distribution on Co.001
 Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
 $H_2:CO=2$, T=210°C, t=24 hrs, CO Conv.=2.60%

Fig. 20 Schulz-Flory Distribution on Co.001
 Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
 $H_2:CO=2$, T=210°C, t=48 hrs, CO Conv.=2.62%

Fig. 21 Schulz-Flory Distribution on Co.001
Conditions: wt=0.1 g, F=50 cc/min, P=1 atm,
H₂:CO=2, T=210°C, t=72 hrs, CO Conv.=2.52%

Figure 22

Slurry Bubble Column Reactor
Catalyst Test Unit

APPENDIX

Co006

20 wt% Co

0.75 wt% Re (Re/Co = 0.012 at. ratio)

TiO₂ [Exxon used P25 Degussa having rutile content of 97%]

Based on Exxon U.S. Patent 4,794,099 (Iglesia, Soled, Fiato) (1988).

Preparation Procedure:

Use TiO₂.

Calcine the TiO₂ at 650°C for 16 hrs (this should result in a support having ca. 97% rutile).

Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an acetone solution of Co nitrate [Co(NO₃)₂·6H₂O] (from) and perrhenic acid (from) using an appropriate quantity to get a slurry with the desired loading of Co and Re. Approximately 0.8 cc of acetone will expand to 1 cc upon solution of the salts.

Dry the catalyst precursor in a rotor evaporator at 25°C and then in vacuum at 140°C for 16 hours.

Calcine in air at 250°C for 3 hours.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to the air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 1000 cc/g/hr by heating to 350°C and holding overnight (for 16 hrs).

Co007

20 wt% Co

TiO₂ [Exxon used P25 Degussa having rutile content of 97%]

Based on Exxon U.S. Patent 4,794,099 (Iglesia, Soled, Fiato) (1988) except without Re.

Preparation Procedure:

Use TiO₂.

Calcine the TiO₂ at 650°C for 16 hrs (this should result in a support having ca. 97% rutile.

Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an acetone solution of Co nitrate [Co(NO₃)₂·6H₂O] (from) using an appropriate quantity to get a slurry with the desired loading of Co. Approximately 0.8 cc of acetone will expand to 1 cc upon solution of the salts.

Dry the catalyst precursor in a rotor evaporator at 25°C and then in vacuum at 140°C for 16 hours.

Calcine in air at 250°C for 3 hours.

Rescreen to remove fines.

Reduction Procedure:

In the original patent it was just stated that the catalyst should be reduced at 250-450°C for 2-14 hours.

However, to be consistent with other catalysts, use the following procedure. Reduce the catalyst using pure hydrogen at a flow rate of 720 cc/g/hr. The impregnated catalyst is heated to 100°C at the rate of 1°C/min and then maintained for 1 hr. Next, the catalyst is heated to 200°C at the rate of 1°C/min and held for 2 hrs. The catalyst is then heated at 10°C/min until a temperature of 360°C is reached and is then held at that temperature for 16 hrs.

If the catalyst will be exposed to air, cool the catalyst below 200°C, purge with nitrogen, and cool further. Air is bled into the nitrogen stream at ca. 1 cc air in 50 cc nitrogen per min per 5 g of catalyst for 16 hours.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 1000 cc/g/hr by heating to 350°C and holding overnight (for 16 hrs).

Co.008: **20 wt% Co**
 SiO₂

Non-promoted catalyst similar otherwise to the Zr-promoted SHELL catalyst based heavily on Hoek, Joustra, Minderhoud, and Post, UK Pat. Appl. GB 2 125 062 A (1983).

denotes deviations from the patent where indicated by or steps not stated in the patent

Bold type indicates steps listed in the patent.

Preparation Procedure:

Calcine the SiO₂ at 500°C for 10 hrs. Presieve to 38-63 microns (400-250 mesh).

Knead a mixture comprised of the support and an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] where the aqueous solution is 150% of the pore volume of the silica. Knead for 3.5 hours.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs. [Note: the patent suggests calcination in air at 500°C.]

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 250°C and holding for 10 hrs.

**Co.010: 20 wt% Co
 γ -alumina**

Non-promoted catalyst similar otherwise to the Re + La-promoted catalyst based on Eri et al., U.S. Pat. No. 4,880,763 (1989).

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

NO CALCINATION !!

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Co.011: **20 wt% Co**
 SiO₂

Non-promoted catalyst similar otherwise to the Zr-promoted SHELL catalyst based heavily on Hoek, Joustra, Minderhoud, and Post, UK Pat. Appl. GB 2 125 062 A (1983).

denotes deviations from the patent where indicated by or steps not stated in the patent

Bold type indicates steps listed in the patent.

Preparation Procedure:

Calcine the SiO₂ at 500°C for 10 hrs. Presieve to 38-63 microns (400-250 mesh).

Knead a mixture comprised of the support and an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] where the aqueous solution is 110% of the pore volume of the silica. Knead for 3.5 hours.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs. [Note: the patent suggests calcination in air at 500°C.]

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 250°C and holding for 10 hrs.

Co.012: **20 wt% Co**
 SiO₂

Non-promoted catalyst similar otherwise to the Zr-promoted SHELL catalyst based heavily on Hoek, Joustra, Minderhoud, and Post, UK Pat. Appl. GB 2 125 062 A (1983).

denotes deviations from the patent where indicated by or steps not stated in the patent

Bold type indicates steps listed in the patent.

Preparation Procedure:

Calcine the SiO₂ at 500°C for 10 hrs. Presieve to 38-63 microns (400-250 mesh).

Impregnate the support with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O], using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs. [Note: the patent suggests calcination in air at 500°C.]

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 250°C and holding for 10 hrs.

END

**DATE
FILMED**

10 / 22 / 93