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## DISCLAIMER



~~FINAL REPORT~~

# TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

**Contract No. DE-AC22-92PC92108**

## QUARTERLY TECHNICAL PROGRESS REPORT NO. 15

Covering the Period April 1, 1996 to June 30, 1996



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# EXECUTIVE SUMMARY

A 3,183-hour long catalyst aging slurry bubble column reactor test run utilizing one of the selected catalysts prepared by Calsicat started on January 8, 1996 was ended on May 20, 1996. The effects of temperature, pressure, and catalyst age on catalyst productivity, product distribution, methane yields, Anderson-Shulz-Flory chain growth probability were determined utilizing one of the bench-scale slurry bubble column reactors. Experimental details about this run as well as the results and conclusions derived from it will be provided in the final report

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## ACKNOWLEDGMENT

The following persons contributed to this report: Rachid Oukaci, William Gall, and Alan Singleton.

## 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

A 3,183-hour long catalyst aging slurry bubble column reactor test run utilizing one of the selected catalysts prepared by Calsicat started on January 8, 1996 was ended on May 20, 1996. The remainder of this reporting period was spent evaluating the data collected during this test run as well as compiling all the data from previous runs for the final report.

## V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

### A. TASK 1: CATALYST DEVELOPMENT

Except for Subtask 1.1 (Technology Assessment), Task 1 has been completed. A topical report on the technology assessment of cobalt catalysts for Fischer-Tropsch synthesis is being drafted in parallel with the final report.

### B. TASK 2: CATALYST TESTING

#### Subtask 2.2 - Slurry Bubble Column Testing (SBCR)

During this reporting period a 3,183-hour long catalyst aging SBCR test run, M3-65, utilizing one of the selected catalysts prepared by Calsicat started on January 8, 1996 was ended on May 20, 1996. The effects of temperature, pressure, and catalyst age on catalyst productivity, product distribution, methane yields, Anderson-Shulz-Flory chain growth probability were

determined utilizing one of the bench-scale slurry bubble column reactors. This work was initially performed as part of Energy International's own F-T technology development outside this contract. It was latter agreed to include the results of this test run in the form of additional reporting in the contract final report. Thus, further experimental details about this run as well as the results and conclusions derived from it will be provided in the final report. The remainder of this reporting period was spent evaluating the data collected during this long test run as well as compiling all the data from previous runs for the final report.

### C. TASK 5: CATALYST PREPARATION FACILITY

A report provided by Calsicat on the final cost estimate for the preparation of 1,000 to 250,000 lb batches of the best catalysts identified in this project will be included in the final report.

## VI. PLANS FOR THE NEXT REPORTING PERIOD

All experimental work for this project has been completed. Further evaluation of all the data collected during the length of this project will be continued with the writing of the final report.

## 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. The project will be completed by September 30, 1996