

## 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<sub>2</sub>/CO ratio syngas because of its lack of water-gas shift activity. The broad objective of this proposal is to overcome these deficiencies.

In pursuing F-T catalyst development, there are several aspects that need to be considered. These are catalyst formulation, catalyst pretreatment, and catalyst performance. All of these aspects will be dealt with in this project.

In broad terms, the technical approach that will be used is outlined below.

- a. Conduct a thorough review of the literature on F-T synthesis, both the journal literature and the patent literature. In this review, identify approaches for improving methane selectivity of cobalt-based catalysts, identify additives that have WGS activity, identify catalyst formulation options, and define critical pretreatment parameters.
- b. Based on the above review, develop a list of catalyst formulations with potential for low methane selectivity and a list of catalyst formulations with potential for promoting the WGS reaction.
- c. Screen these catalysts in a small, fixed-bed reactor. If no catalyst meets the target specifications, go back to step b. Otherwise, run catalysts that meet discrimination criteria in a slurry bubble column reactor.
- d. Once catalysts with low methane selectivity and WGS activity have been identified, develop a catalyst combining both these functions and test as described above.
- e. Having found catalysts that meet the desired criteria for activity and selectivity, optimize the pretreatment conditions.

- f. Demonstrate catalyst reproducibility by having a commercial subcontractor prepare multiple batches for testing.
- g. Demonstrate catalyst stability by running aging tests in a slurry bubble column reactor.
- h. Based on above results, prepare a design for a plant to produce demonstration scale batches of catalyst. Develop capital and operating costs of this plant.

The program to carry out the above outlined work will consist of five major tasks:

Task 1 -- Catalyst Development

Task 2 -- Catalyst Testing

Task 3 -- Catalyst Reproducibility Tests

Task 4 -- Catalyst Aging Tests

Task 5 -- Preliminary Design and Cost Estimate for a Demonstration Scale

#### Catalyst Production Facility

All aspects of the catalyst's role in F-T processing will be addressed, including catalyst preparation, pretreatment, and performance (activity, selectivity, and aging). In addition to gathering process data, the catalyst will be subjected to a number of analytical measurements at each stage to see how various treatments have affected the catalyst and its performance.

### III. OBJECTIVES

The objective of this project is to investigate the influence of various promoters, additives, and supports on minimizing the methane selectivity and increasing the water-gas shift (WGS) activity of cobalt (Co) Fischer-Tropsch (F-T) catalysts. The ultimate goal of this investigation is

to identify and demonstrate a catalyst preparation procedure that will be scaled up for the reproducible synthesis of commercial quantities of supported CO catalysts with desired activity, selectivity, and lifetime for use in F-T synthesis in three-phase slurry bubble column reactors.

#### IV. SUMMARY OF WORK ACCOMPLISHED THIS QUARTER

Two new non-promoted Co/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by Calsicat during this reporting period following the formulation used previously for Co.005. The main difference between these two catalysts was in the procedure used for their reduction.

Two runs were performed in the slurry bubble column reactor to evaluate the performance of these two catalysts and the effectiveness of the procedures used for reduction.

#### V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

##### A. TASK 1: CATALYST DEVELOPMENT

###### 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 7 with their compositions. Two new catalysts were prepared by Calsicat during this period following the formulations used previously for Co.005 (CAL.27-CAL.28). The main difference between these two catalysts was in the procedure used for their reduction. Following the unsuccessful reduction of large batches of the non-promoted catalysts and the belief that the large amount of water produced during the initial stages of reduction was responsible for their low reducibility, it was suggested that higher reduction temperatures may improve their reducibility. Hence, two new small batches of the unpromoted catalysts were reduced at 410°C (CAL.27) and

380°C (CAL.28). In order to simulate the commercial reduction procedure where part of the effluent moist hydrogen would be recycled, the hydrogen stream used for reduction was saturated with water vapor at room temperature by passing it through a saturator before reaching the reduction system. The catalysts were also flaked in soya wax for easier handling and shipment in a reduced state.

## B. TASK 2: CATALYST TESTING

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

During this reporting period a total of 2 runs were performed in the SBCR's, Runs M4-52 and 53. Both runs (4052 and 4053 in Table 13) were made in the M4-SBCR at standard conditions, but at a lower reaction temperature, 220°C using the two catalysts provided by Calsicat.

Run 4052 was started with a charge of 15 gm of catalyst CAL.27. This catalyst was reduced at 410°C in moist H<sub>2</sub> and passivated by flaking in soya wax. Run 4053 was started with a charge of 15 gm of catalyst CAL.28. This catalyst was also reduced in moist H<sub>2</sub> at 380°C and flaked in soya wax. Both catalysts had very low activity with < 1% CO conversion. The results show that the high temperature reductions of non-promoted Co/Al<sub>2</sub>O catalysts did not improve their reducibility. It even had a negative effect. The high concentration of water in the hydrogen stream is believed to enhance the formation of cobalt-alumina compounds more difficult to reduce. High temperature seems to enhance this process rather than the reduction.

A complete summary of all runs made in the M3-SBCR is given in Table I in Appendix A. Four tables of data 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 A).

A complete summary of all runs made in the M4-SBCR is given in Table VI, in Appendix

A. Four tables were prepared to compare catalyst activities for Runs 3 to 53 in M4-SBCR at the same run conditions (see Tables VII, VIII, IX, and X in Appendix A).

C. TASK 5: CATALYST PREPARATION FACILITY

Calsicat has reported a preliminary cost estimate for the preparation of 1,000-250,000 lb batches of the best catalysts identified in other tasks of this project. Further discussions between EI and Calsicat have provided the basis for their preliminary estimates. A breakdown reflecting the cost of the various unit operations constituting the commercial process of Co catalysts manufacture was provided by Calsicat. Possible changes in the processes involved were discussed in relation to the commercial scale-up of the preparation of these catalysts. Calsicat shall report a final cost estimate reflecting this cost breakdown into unit operations costs.

VI. PLANS FOR THE NEXT REPORTING PERIOD

Final runs will be made in the SBCR in order to complete this project. 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. The project will be completed by September 30, 1996.

Table 1. List of Co-based FT Catalysts Formulated

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.001	20%	1% Re	1% La <sub>2</sub> O <sub>3</sub> 0.13% K	γ-alumina	U.S. Pat. 4,880,763	P
Co.002	20%	0.43% Ru	1% La <sub>2</sub> O <sub>3</sub>	γ-alumina	U.S. Pat. 4,413,064	P
Co.003	20%	0.5% Ru	1% La <sub>2</sub> O <sub>3</sub>	γ-alumina	U.S. Pat. 4,413,064	P
Co.004	20%	0.43% Ru	1% La <sub>2</sub> O <sub>3</sub>	γ-alumina	Reproduce Co.002	P
Co.005	20%	0.00	0.00	γ-alumina	Base Catalyst	P
Co.005A	20%	0.4% Ru	0.00	γ-alumina	Ru added to calcined Co.005 by IW impreg.	P
Co.006	12%	0.75% Re	0.00	Titania	U.S. Pat. 4,794,009	P
Co.007	20%	0.00	0.00	Titania	Base Catalyst	P
Co.008	20%	0.00	0.00	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded with excess liquid)	P
Co.009	20%	0.5% Ru	0.00	γ-alumina	Ru-Promoted Catalyst (use Ru Chloride, single-step aqueous IW)	P
Co.010	20%	0.00	0.00	γ-alumina	Base Catalyst (non-calcined)	P
Co.010A	20%	0.4% Ru	0.00	γ-alumina	Ru added to dried Co.010 by IW impreg.	P
Co.011	20%	0.00	0.00	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded)	P
Co.012	20%	0.00	0.00	Silica	Base Catalyst (Inc. Wetness)	P
Co.013	20%	0.00	0.00	Titania	Base Catalyst like Co.007, but all aqueous	P
Co.014	12%	0.5% Ru	0.00	Titania	Ru-Promoted Catalyst (aqueous IW co- impregnation)	P
Co.015	20%	0.43% Ru	1% La <sub>2</sub> O <sub>3</sub>	γ-Alumina	Similar to Co.002, but all aqueous	P

Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.016	20%	0.43% Ru	1% La <sub>2</sub> O <sub>3</sub>	$\gamma$ -Alumina	Similar to Co.015, but calcined after Co impregnation	P
Co.017	20%	0.5% Ru	1% La <sub>2</sub> O <sub>3</sub>	$\gamma$ -Alumina	Similar to Co.003, but all aqueous	P
Co.018	20%	0.5% Ru	0.00	$\gamma$ -Alumina	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.019	20%	0.5% Ru	0.00	Silica	Ru-Promoted Catalyst (single-step, aqueous IW)	P
Co.020	0.00	0.5% Ru	0.00	$\gamma$ -Alumina	Ru Base Catalyst	P
Co.020A	20%	0.4% Ru	0.00	$\gamma$ -Alumina	Co added to dried Co.020 by IW impreg.	P
Co.020B	20%	0.4% Ru	0.00	$\gamma$ -Alumina	Co added to reduced Co.020 by IW impreg.	P
Co.020C	20%	0.4% Ru	0.00	$\gamma$ -Alumina	Co added to calcined Co.020 by IW impreg.	P
Co.021	20%	0.00	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (single-step, aqueous kneaded)	P
Co.022	20%	0.00	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (aqueous, multiple-steps, kneaded Co pre-impregnation, IW Zr)	P
Co.023	20%	0.00	1.4% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (aqueous, multiple-steps, kneaded Co pre-impregnation, IW Zr)	P
Co.024	20%	0.00	8.5% Zr	Silica	Eur. Pat. Appl. 0 167 215 A2 (non-aqueous, IW, multiple-steps, Zr pre-impregnation)	P
Co.025	20%	0.00	8.5% Zr	Silica	Similar to Co.024 but aqueous Zr pre-impregnation	P



Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.026	20%	0.00	0.00	Silica (Davison Grade 59)	Similar to Co.012 but different grade silica	P
Co.027	20%	0.5% Ru	0.00	Silica (Davison Grade 59)	Similar to Co.019 but different grade silica	P
Co.028	20%	0.5% Ru	0.5% K	$\gamma$ -alumina	Ru- and K-Promoted Catalyst (single-step IW)	P
Co.029	30%	0.5% Ru	0.5% K	$\gamma$ -alumina	Similar to Co.028 but 30% Co	P
Co.030	20%	0.00	0.1% Zr	$\gamma$ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.031	20%	0.00	1.4% Zr	$\gamma$ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.032	20%	0.00	8.5% Zr	$\gamma$ -alumina	Zr-Promoted Catalyst (single-step aqueous IW)	P
Co.033	20%	0.00	8.5% Zr	$\gamma$ -alumina	Multiple-steps, aqueous IW, Co pre-impregnation	P
Co.034	20%	0.00	8.5% Zr	$\gamma$ -alumina	Multiple-steps, aqueous IW, Zr pre-impregnation	P
Co.035	20%	0.00	8.5% Zr	Silica	Zr-Promoted Catalyst (single-step aqueous, kneaded)	P
Co.036	20%	0.00	8.5% Zr	Silica	Multiple-steps, aq. Co pre-impreg. by kneading, aqueous IW Zr impreg.	P
Co.037	12%	0.00	0.00	Titania	Similar to Co.013, but TiO <sub>2</sub> mainly anatase	P
Co.038	12%	0.5% Ru	0.00	Titania	Similar to Co.014, but TiO <sub>2</sub> mainly anatase	P
Co.039	12%	0.00	0.00	Titania	Similar to Co.007, but only 12% Co	P
Co.040	12%	0.00	0.00	Titania	Similar to Co.013, but only 12% Co	P
Co.041	20%	0.5% Ru	8.5% Zr	Silica	Similar to Co.025, but Ru-promoted	P

Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.042	0.00	0.00	8.5% Zr	Silica	Blank Zr-promoted SiO <sub>2</sub>	P
Co.043	20%	0.5% Ru	8.5% Zr 0.5% K	Silica	Similar to Co.041, but K-promoted	P
Co.044	20%	0.00	15% Zr	Silica	Similar to Co.025, but 15% Zr	P
Co.045	20%	0.00	4% Zr	Silica	Similar to Co.025, but 4% Zr	P
Co.046	12%	0.75% Re	4% SiO <sub>2</sub>	Titania	Similar to Co.006, but SiO <sub>2</sub> -promoted	-
Co.047	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.028, but 0.3% K	P
Co.048	20%	0.5% Ru	8.5% Zr 0.3% K	Silica	Similar to Co.043, but 0.3% K	P
Co.049	20%	0.5% Ru	0.1% K	$\gamma$ -alumina	Similar to Co.047, but 0.1% K	P
Co.050	20%	0.5% Ru	8.5% Zr 0.1% K	Silica	Similar to Co.048, but 0.1% K	P
Co.051	0.00	0.5% Ru	0.00	Titania (R)		P
Co.052	0.00	0.5% Ru	0.00	Titania (A)		P
Co.053	20%	0.5% Ru	0.00	$\gamma$ -alumina	Similar to Co.018 (New Batch)	P
Co.054	20%	0.00	8.5% Zr 0.3% K	Silica	Similar to Co.043, but without Ru	P
Co.055	20%	1% Re	1% La <sub>2</sub> O <sub>3</sub>	$\gamma$ -alumina	Similar to Co.001, but without K	P
Co.056	20%	0.00	8.5% La <sub>2</sub> O <sub>3</sub>	Silica	Similar to Co.025, but La instead of Zr	P
Co.057	20%	1% Re	1% La <sub>2</sub> O <sub>3</sub>	Silica	Similar to Co.055, but with SiO <sub>2</sub> support	P
Co.058	20%	0.00	1% La <sub>2</sub> O <sub>3</sub>	$\gamma$ -alumina	Similar to Co.055, but without Re (one-step impreg.)	P
Co.059	20%	0.00	1% La <sub>2</sub> O <sub>3</sub>	$\gamma$ -alumina	Similar to Co.015, but without Re (two-step impreg.)	P
Co.060	30%	0.00	0.00	$\gamma$ -alumina	Similar to Co.005, but with 30% Co	P
Co.061	30%	0.5% Ru	0.00	$\gamma$ -alumina	Similar to Co.053, but with 30% Co	P

Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.062	30%	0.5% Ru	1.5% K	$\gamma$ -alumina	Similar to Co.029, but with 1.5% K	P
Co.063	20%	0.00	8.5% La	$\gamma$ -alumina	Multiple-steps, aqueous IW, La pre-impregnation	P
Co.064	20%	0.5% Ru	8.5% Zr	$\gamma$ -alumina	Multiple-steps, aqueous IW, Zr pre-impregnation	P
Co.065	20%	0.5% Ru	8.5% Zr 0.3% K	$\gamma$ -alumina	Multiple-steps, aqueous IW, Zr pre-impregnation	P
Co.066	15%	0.5% Ru, 5.0% Fe	0.00	$\gamma$ -alumina	Ru- and Fe-Promoted Catalyst (single-step, aqueous IW)	P
Co.067	20%	2.0% Pd	0.00	$\gamma$ -alumina	Pd-Promoted Catalyst (single-step, aqueous IW)	P
Co.068	20%	1.0% Pd	0.00	$\gamma$ -alumina	Similar to Co.067, but with 1% Pd	P
Co.069	20%	2.0% Ru	0.00	$\gamma$ -alumina	Similar to Co.053, but with 2% Ru	P
Co.070	13%	0	0.00	$\gamma$ -alumina	Similar to Co.005, but with 13% Co	P
CAL.01 (97E-13E)	20%	0.5% Ru	0.00	$\gamma$ -alumina	Similar to Co.018 (Calsicat Prep.)	P
CAL.02 (97E-16B)	20%	0.5% Ru	0.00	$\gamma$ -alumina	Similar to CAL.01 (New Batch)	P
CAL.03 (97E-13F)	20%	0.5% Ru	0.00	$\gamma$ -alumina	Multiple-step impreg., Similar to CAL.02	P
CAL.04 (97E-50C)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.047 Stand. Calc. in Air	P
CAL.05 (97E-50D)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.047 Stand. Calc. in N <sub>2</sub>	P
CAL.06 (97E-51A)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.047 Red. and Pas. in Air	P
CAL.07 (97E-51B)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.047 Red. and Protected in Paraffin (51.3% Cat. Conc.)	P
CAL.08 (97E-51C)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to Co.047 Calc., Red. and Protected in Paraffin (54.4% Cat. Conc.)	P

Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
CAL.09 (97E-69C)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.05, Reduced and Protected in Soya (51.7% Cat. Conc.)	P
CAL.10 (97E-79A)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina (Condea)	Similar to CAL.05, but on Condea $Al_2O_3$	P
CAL.11 (29F-07B)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.05	P
CAL.12 (29F-05D)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.05	P
CAL.13 (29F-07E)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.05	P
CAL.15 (29F-38B)	20%	0.00	0.00	$\gamma$ -alumina	Similar to Co.005, Reduced and Protected in Soya Wax	P
CAL.16 (29F-3D)	20%	0.00	0.00	$\gamma$ -alumina	Similar to Co.005, Reduced and Protected in Soya Wax	P
CAL.17 (29F-39E)	20%	0.00	0.00	$\gamma$ -alumina	Similar to Co.005, Reduced and Protected in Soya Wax	P
CAL.18 (29F-40C)	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.13	P
CAL.19 (29F-39A)	20%	0.00	0.00	$\gamma$ -alumina	Similar to CAL.15, 16 and 17, Reduced at EI under standard conditions	P
CAL.20 (29F-39A,B,C)	20%	0.00	0.00	$\gamma$ -alumina	Similar to CAL.19, Reduced at EI in large batch	P
CAL.24	20%	0.00	0.00	$\gamma$ -alumina	CAL.20 Re-reduced twice at EI using standard conditions	P
CAL.25	20%	0.5% Ru	0.3% K	$\gamma$ -alumina	Similar to CAL.018, but reduced and passivated in Synfluid	P
CAL.27 (29F-41F)	20%	0.00	0.00	$\gamma$ -alumina	Similar to CAL.15, reduced at 410°C in a moist $H_2$ stream	P

Table 1. List of Co-based FT Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
CAL.28 (29F-41E)	20%	0.00	0.00	$\gamma$ -alumina	Similar to CAL.15, reduced at 380°C in a moist H <sub>2</sub> stream	P
Fe.01	0%	30%Fe	1.5%Cu	Silica		P

Table 2

## SUMMARY OF ADDITIONAL M4 SBCR RUN RESULTS

a) Unless otherwise noted, total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

Flows: N2-563 SLH, H2-225 SLH, CO-112 SLH

b) Conversion is total CO conversion over the period (%).

c) Conversion and selectivities are calculated using N2 as an internal standard in the GC analysis of the offgas.

d) Prod. rate: Rate for production of total hydrocarbons, C1+ (kg/kg cat., hr).

e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt, g	Per No	Time Start	Time Stop	Temp C	Pres psi	H2: CO	Synfl cc/hr	Conv. %	Prod. Rate	Selectivities					Alpha GC	Alpha Liq	Comments
												%CH4	%C2	%C3+	%CO2				
4052	CAL.27	15	1	18	22	220	450	2.0	20	<1.0	0.02	-	-	100	-	-	-	-	(1)
4053	CAL.28	15	1	13	15	220	450	2.0	20	0.5	0.03	-	-	100	-	-	-	-	(2)

Notes: (1) Wet reduced at 410o C. and flaked in Soya wax.

(2) Wet reduced at 380o C. and flaked in Soya wax.