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TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS

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Prepared for
U.S. Department of Energy
Pittsburgh Energy Technology Center
PETC Project Manager: Arun Bose
P. O. Box 10940
Pittsburgh, PA 15236-0940

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

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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 H₂/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
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

Review and evaluation of both the open and patent literature as well as the drafting of a preliminary report on the review of Co F-T literature continued during this reporting period.

The formulations of 9 new catalysts were established. Fourteen new catalysts (of the 35 which have been formulated so far) were prepared during this period.

Elemental analysis of several of the calcined catalysts has been carried out. Their physical properties (BET surface area, pore volume, pore size diameter, particle size distribution) have been determined. Cobalt dispersion was determined by both static H₂ chemisorption and XRD.

Fixed bed testing of the catalysts was continued. Five new catalysts have been tested during this reporting period. A new reaction start-up procedure has been adopted in order to avoid significant increases in temperature observed previously with several catalysts when the reaction was started. Some catalysts have been retested using this new start-up procedure.

An investigation of the effect of water partial pressure on the catalytic properties of Co

by addition of water during steady-state F-T synthesis was started.

Under subtask 2.2 in the slurry bubble column reactor six runs were made during this period, using four alumina-based catalysts (i.e. Co.015, Co.016, Co.017, Co.018) and two silica-based catalysts (i.e. Co.011, Co.012). Catalyst formulations are shown in Table 1. Data were compared at specific, selected run conditions with the purpose of determining optimum conditions and optimum formulations. The silica-supported catalysts yielded significantly lower methane selectivities, but also yielded lower CO conversions. As expected, the catalyst particle size was shown to be significant in the catalyst activity. Smaller catalyst particle sizes produced higher CO conversions. All future catalysts will be screened to eliminate particles larger than 100 microns in diameter.

Catalysts have been recovered from the runs and particle size distributions were measured in order to determine attrition levels. All of the alumina-supported catalysts showed little or no attrition while the silica-supported catalysts showed about a 10% reduction in size. Additional chemical analyses will be performed on selected recovered catalysts.

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. TASK 1: CATALYST DEVELOPMENT

a. Technology Assessment (Subtask 1.1)

Review and evaluation of both the patent and open literature as well as the drafting of the preliminary report on this literature review were continued.

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

An updated list of all the catalysts formulated so far (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. Nine new Co catalysts (highlighted in Table 1) have been formulated during this period. Fourteen (14) of the catalysts listed in Table 1 have been prepared during the same period. The detailed formulations of the new catalysts are given in Appendix A.

The new formulations include a series of five Ru-promoted Co on Al_2O_3 catalysts prepared by sequential impregnation with either Ru (Co.020A, Co.020B, Co.020C) or Co (Co.005A and Co.010A) put first on the support followed by different pretreatments of the precursor obtained from this first impregnation (drying, calcination, or reduction). These five Ru-promoted Co catalysts as well as those previously prepared by co-precipitation (Co.009 and Co.018) will be characterized mainly by TPR and hydrogen chemisorption and tested in the fixed-bed reactor in order to determine the effects of noble metal promotion and establish the optimum method of incorporating such promoters into the catalyst precursor.

Co.026 and Co.027 have been formulated in order to investigate the effect of different grades of silica. The previous silica-supported Co catalyst formulations used only Davison Grade 952 silica as the support. Davison grade 59 is used in the formulations of Co.026 and Co.027.

The main objectives with the formulations of Co.028 and Co.029 are (a) to investigate the effect of Co loading and (b) the effect of potassium promotion on the properties of Co catalysts.

As reported in the previous quarterly report and as shown in Table 1, several catalysts using TiO_2 as a support have not yet been prepared. These formulations were based on a number of patents assigned to Exxon. The titania used in the patents (Degussa P25) requires further pretreatment in order to obtain a desirable particle size range suitable for use in a slurry bubble column reactor. As received, the titania has an average particle diameter of $6\ \mu\text{m}$. In addition, the P25 titania was received in its anatase form which is not suitable for slurry bubble column application because of its low resistance to attrition. A pretreatment of the titania was also required to convert it to the more attrition resistant rutile phase. The calcination conditions given in the patents did not seem to result in the required particle size range nor the conversion of anatase to rutile. Thus, a pretreatment study of P25 titania was undertaken in order to determine the suitable conditions which produce a titania support with the suitable composition and in the required particle size range (see Subtask 1.5). The preparation of the formulated Co/ TiO_2 catalysts will be completed in the next reporting period.

c. Catalyst Pretreatment (Subtask 1.5)

A pretreatment study of P25 titania was carried out in order to determine the suitable conditions which produce a titania support with the suitable composition and in the required particle size range. Various calcination temperatures as well as pre-wetting followed by drying at various temperatures have been tried. Particle size and XRD measurements were used to characterize the pretreated titania. Wetting of the titania followed by drying and calcination resulted in ca. 100% conversion of anatase to rutile at any calcination temperature above ca. 650°C. However, in order to obtain the desired particle size range drying at low temperature (ca. 60°C) with occasional stirring was required.

The pretreatment conditions that seem to give the best result were established, i.e., wetting then drying in air at 60°C with occasional stirring followed by calcination at 650°C.

d. Catalyst Characterization (Subtask 1.6)

(1) Elemental Analysis

The composition of several catalysts in their calcined form has been determined by ICP (Inductively Coupled Plasma Atomic Emission Spectroscopy). The results are shown in Table 2. The results are in agreement with the nominal compositions (based on the reduced metals) given in Table 1.

(2) 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. BET measurements for a series of Vista-B alumina calcined at different temperatures are also included in Table 3. Average particle size of the catalysts was

determined using a Microtrac particle size analyzer.

(3) XRD Measurements

An updated summary of the XRD measurements for the cobalt Co is given in Table 4. The new XRD patterns for the Co catalysts and for the titania and the Vista-B alumina after different pretreatment conditions are shown in Appendix B.

(4) Static Hydrogen Chemisorption

Table 5 summarizes the properties of these catalysts as determined by H₂ chemisorption. Static H₂ chemisorption isotherms for Co catalysts measured during this reporting period are plotted in Appendix B.

B. TASK 2: CATALYST TESTING

a. Subtask 2.1 - Fixed Bed Reaction Studies:

The reaction conditions and procedure were described in the previous quarterly report. However, due to the unexpectedly high methane selectivity obtained for some FT runs (Co.002 runs #1 and 2, Co.017 run #1) the start-up procedure of the reaction was modified.

Initially, the reaction was started in the following way. The catalyst was re-reduced *in-situ* in the reactor and cooled to reaction temperature (usually 220°C) under hydrogen flow. Hydrogen was subsequently replaced by the reactant feed consisting of a 2:1 H₂/CO mixture. In certain cases (in particular with Al₂O₃ supported, higher activity catalyst), a significant increase in catalyst bed temperature was observed which was attributed to high initial reaction rates. The exothermicity and the observed increase in temperature could lead to modifications of the catalyst (i.e., sintering) and, thus, had to be avoided.

In a first improvement, the CO concentration was gradually increased over a time period of 30 to 120 minutes up to the desired level. Although the initial heat generation was substantially reduced, the high initial hydrogen concentration on the catalyst surface and in the reactant feed still caused a notable increase in reaction temperature during the initial stages of reaction. This was reflected in generally higher methane selectivity, lower reaction rates and reduced chain growth probability as compared to the second modification for the start-up procedure.

In order to overcome the high initial hydrogen concentrations, the catalyst was purged with helium (argon) after *in-situ* reduction and cooling to reaction temperature for 30 minutes. This step effectively removes adsorbed hydrogen from the catalyst surface. Then, the reactant feed was admitted consisting of a mixture of Ar:H₂:CO (30:4:2). The concentration of H₂ and CO was then gradually increased at a constant ratio of H₂:CO = 2:1 while simultaneously decreasing the argon concentration, thus, avoiding high hydrogen concentrations (and high H₂:CO ratios) in the gas phase. The desired feed concentrations were reached after 2 hours. This procedure gave no measurable exothermicity and better and more reliable results.

Five new catalysts (Co.015-Co.019) were tested during this reporting period. Catalysts Co.015 and Co.016 were not tested with the new start-up procedure. Catalysts Co.002 and Co.005 were also retested using the new start-up procedure. All the previously tested catalysts will eventually be rerun using this new start-up procedure in order to compare all the catalysts under the same conditions.

The performances of all these catalysts at steady state are compared in Table 6 with those reported in the previous quarterly report. All the pertinent data (CO conversion, rates, product distributions, chain growth probabilities, Anderson-Schulz-Flory distributions, and Arrhenius plots) obtained with each run for each catalyst (Co.002, Co.005 and Co.015-Co.019) is given in Appendix C.

Water Addition during CO Hydrogenation in Fixed Bed Reaction System

According to recent reports and communications the effect of promoters may be leveled out (masked) at higher CO conversions due to the presence of considerable amounts of water (formed during the CO hydrogenation reaction). In order to test for this effect we carried out some experiments in which the addition of water was used to artificially simulate water levels at "high CO conversion".

A jacketed glass saturator connected to a recirculating thermostat was used to feed the water. The saturator was filled with boiling water (for removal of absorbed oxygen) and purged with argon during cooling. Argon was also used as carrier gas for the reaction and the concentration of water in the reactant feed was controlled by the saturator temperature and the various flows of the feed components (H_2 , CO, Ar/ H_2O). Initially, water concentrations equivalent to the amount that would be produced by ca. 7.5% CO conversion was used. Two catalysts (Co.005 and Co.017) were tested with the water addition during steady-state FT synthesis. The results are highlighted in Table 6 and the pertinent data for these reactions is also included in Appendix C. At the relatively low water partial pressure (0.016 atm) used, no significant effect of water was observed. Further studies will be carried out with higher water concentrations equivalent to amounts obtained with ca. 25% CO conversion (i.e., comparable

to the conversions achieved in the slurry bubble column reactor).

(b) Subtask 2.2 - Slurry Bubble Column Testing

1. Run Chronology

Run No. 7 was started on July 6, 1993 and was completed on July 16th after following the run strategy established during the second quarter. A total of 15.8 gm of Catalyst No. Co.012 (20 wt% cobalt on silica support with no promoters) had been charged. The CO conversion was about one half of that obtained when using alumina supported catalysts (see Table I in Appendix D). This catalyst is similar to Catalyst No. Co.011 which was used for Run 6, but was prepared in a single step with aqueous kneading while Catalyst Co.012 was prepared in a single step with the aqueous incipient wetness preparation method. No significant difference in catalyst activity was observed between these two catalysts.

Run No. 8 was started on July 20th, but was completed prematurely after Period No. 5 on July 28, 1993 when a major power outage occurred. A total of 15.0 gm of Catalyst No. Co.015 had been charged, which is the same as Catalyst No. Co.002 (Run 4), 20% Co, 0.43% Ru, and 1% La₂O₃, but was prepared in all aqueous steps. The CO conversion was the same for both catalysts on a per-gram-charged basis, but the C₆+ production rate was higher, 790 g/Kg cat/hr for Co.015 vs. 500 g/Kg cat/hr for Co.002. Also, the CH₄ selectivity was lower for Co.015, 12.7% vs. 22.9%. Run No. 4 will be repeated since it was terminated after only 149 hours when a major power outage occurred.

Run No. 9 was started on August 2nd and completed on August 12th. A total of 15.0 gm of Catalyst No. Co.011 had been charged. This was the same catalyst used for Run No. 6

except it was rescreened to 400 x 170 mesh to remove particles larger than 100 microns in diameter. The CO conversion was higher, 18.5% vs. 14.3% at the initial startup run conditions (see Table I, Runs 6 and 9 and also Table II in Appendix D). The methane selectivity increased slightly, 7.6% to 8.8%. The increase in catalyst activity can be attributed to the smaller catalyst size which had been demonstrated in earlier SBCR reaction studies. All future catalysts will be screened to this smaller particle size range before charging to the SBCR.

Run No. 10 was started on August 24, 1993, with a charge of 15.5 gm of catalyst No. Co.016. This catalyst is similar to Catalyst No. Co.015 (20% Co, 0.43% Ru, and 1% La₂O₃ on alumina support) but was calcined after Co impregnation. Shortly after the run startup, the hydrogen supply to our laboratory was interrupted for about 8 hours because of a problem with the main supply compressor. After the flow was restored, the CO conversion was only about 75% of the expected value. Since only carbon monoxide and nitrogen were being fed to the reactor with no hydrogen, it was felt that the catalyst was probably damaged, so the run was terminated. This run will be repeated as Run 13.

Run No. 11 was started on August 30, 1993, with a charge of 15.0 gm of Catalyst No. Co.017. This catalyst is the same as Co.015 and Co.016, but was prepared in a single step, aqueous incipient wetness procedure. The CO conversion and product selectivities were very similar to those obtained with Catalyst No. Co.015 (see Runs 8 and 11 on Table I).

Run No. 12 began on September 13th, with a charge of 15.6 gm of Catalyst No. Co.018. This catalyst contained 20% Co and 0.5% Ru on alumina support, but no La₂O₃ promoter. This catalyst yielded a slightly higher CO conversion and C₆+ production rate. The CH₄ selectivity was lower, 9.7% vs. 12.7%, with a corresponding increase in C₂-C₅ yield, 33.2% vs. 28.5%.

The liquid alpha values, however, were very similar. This is the most promising catalyst so far for producing lower methane at a high carbon monoxide conversion level.

2. Discussion of Results

Data for Runs 5 to 12 are compiled on 8 tables and 5 figures found in Appendix D.

Five tables of data were prepared to list the comparison of catalyst activities for Runs 5 through 12 at the same run conditions (see Tables III, IV, V, VI and VII in Appendix D).

Comparison data at 240°C temperature, 450 psi pressure, and H₂/CO ratio of 2/1 are given in Tables III and IV in Appendix D. CO conversions range from 27.2% to 33.8% and the CH₄ selectivity ranges from 9.79 to 16.2% for the alumina-supported catalysts. Catalyst No. Co.018 yielded the lowest CH₄ selectivity for the alumina-supported catalysts while producing the highest CO conversion. The silica-supported catalysts produced the lowest CH₄ selectivities, but gave much lower CO conversions.

The catalyst activities at 220°C temperature, 450 psi pressure, and 2/1 H₂/CO ratio are given in Table V. As expected, the CO conversions are lower and the CH₄ selectivities follow the same trend as in Table IV in Appendix D. The liquid product alpha values are higher at the lower temperature.

The CO conversions are slightly higher at 240°C, 450 psi, and 1/1 H₂/CO ratio (see Table VI in Appendix D). The CH₄ selectivities were similar to those at 220°C (Table V) but the olefin content of the C₃s and C₄s increased significantly.

Raising the reaction pressure to 600 psi while holding the reaction temperature at 240°C with a 1/1 H₂/CO feed ratio only increased the CO conversion slightly (see Table VII in Appendix D). The olefin content of the C₆-C₁₈ products, however, increased significantly, 30%

vs. 20% obtained at Period 1 conditions. All data for future runs will be tabulated using this format to show comparisons of catalyst activity at similar run conditions.

3. Catalyst Recovery Analyses

The catalysts charged for all runs have been recovered and the particle size distributions have been measured. The charge and recovered weights of all catalysts are given in Table VIII. The charge weights are in the H₂ 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 diameter of both the charged and recovered catalysts are also given in Table VIII in Appendix D. In general, all the alumina-supported catalysts (except Co.005) showed little or no attrition during the reaction. The silica-supported catalysts (Co.011 and Co.012) did show about 10% reduction in size. Additional chemical analyses will be performed on all the recovered catalysts.

VI. 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. The catalysts that had already been tested using the old reaction start-up procedure will be retested in order to compare all the catalysts under the same conditions.

A comparative study of all the patented (benchmark) catalysts will be carried out, once they have all been tested under the same conditions and characterized.

A study of the effects of noble metal promoter and the way these promoters are incorporated into the catalyst precursor will be started.

(b) The systematic characterization of all the benchmark, base, and modified 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).

(c) The drafting of a preliminary review of the Co F-T literature will be continued.

(d) New catalyst formulations will be generated in order to pursue the effect of selectivity promoters. The formulation of water-gas shift catalysts which would eventually be incorporated or integrated into Co FT catalysts will be established for start-up of Task 1.3.

(e) Other benchmark catalysts shall be hydrogen-reduced and charged for the next runs in the slurry bubble column reactor, using the same run-program strategy as used previously.

(f) Testing of more catalysts in the SBCR.

(g) An uninterruptible power supply unit will be purchased and installed to protect the SBCR's data acquisition system from power failure.

VII. ASSESSMENT OF PROSPECTS FOR FUTURE PROGRESS

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

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	P
Co.004	20%	0.43% Ru	1% La ₂ O ₃	γ -alumina	Reproduce Co.002	P
Co.005	20%	0	0	γ -alumina	Base Catalyst	P
Co.005A	20%	0.4% Ru	0	γ -alumina	Ru added to calcined Co.005 by IW impreg.	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 (Kneaded with excess liquid)	P
Co.009	20%	0.5% Ru	0	γ -alumina	Ru-Promoted Base Catalyst (use Ru Chloride)	P
Co.010	20%	0	0	γ -alumina	Base Catalyst (non-calcined)	P
Co.010A	20%	0.4% Ru	0	γ -alumina	Ru added to dried Co.010 by IW impreg.	P
Co.011	20%	0	0	Silica	UK Pat. Appl. GB 2 125 062 A (Kneaded)	P
Co.012	20%	0	0	Silica	Base Catalyst (Inc. Wetness)	P
Co.013	20%	0	0	Titania	Base Catalyst like Co.007, but all aqueous	-
Co.014	20%	0.5% Ru	0	Titania	Ru-Promoted Base Catalyst (aqueous)	-
Co.015	20%	0.43% Ru	1% La ₂ O ₃	γ -Alumina	Similar to Co.002, but all aqueous	P
Co.016	20%	0.43% Ru	1% La ₂ O ₃	γ -Alumina	Similar to Co.015, but calcined after Co impregnation	P

Table 1. List of Catalysts Formulated (contd.)

CAT. NO.	wt% Co	wt% M	wt% Prom.	Support	Basis	Prepared
Co.017	20%	0.5% Ru	1% La ₂ O ₃	γ -Alumina	Similar to Co.003, but all aqueous	P
Co.018	20%	0.5% Ru	0	γ -Alumina	Ru-Promoted Base Catalyst (aqueous)	P
Co.019	20%	0.5% Ru	0	Silica	Ru-Promoted Base Catalyst (aqueous)	P
Co.020	0	0.5% Ru	0	γ -Alumina	Ru Base Catalyst	P
Co.020A	20%	0.4% Ru	0	γ -Alumina	Co added to dried Co.020 by IW impreg.	P
Co.020B	20%	0.4% Ru	0	γ -Alumina	Co added to reduced Co.020 by IW impreg.	P
Co.020C	20%	0.4% Ru	0	γ -Alumina	Co added to calcined Co.020 by IW impreg.	P
Co.021	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 15 062 A (single-step)	P
Co.022	20%	0	0.7% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.023	20%	0	1.4% Zr	Silica	U.K. Pat. Appl. GB 2 125 062 A (multiple-steps)	P
Co.024	20%	0	8.5% Zr	Silica	Eur. Pat. Appl. 0 167 215 A2 (non-aqueous Zr pre-impregnation)	-
Co.025	20%	0	8.5% Zr	Silica	Similar to Co.024 but aqueous Zr pre-impregnation	P
Co.026	20%	0	0	Silica (Davison Grade 59)	Similar to Co.012 but different grade silica	-
Co.027	20%	0.5% Ru	0	Silica (Davison Grade 59)	Similar to Co.019 but different grade silica	-
Co.028	20%	0.5% Ru	0.5% K	γ -alumina	Ru- and K-Promoted Base Catalyst	P
Co.029	30%	0.5% Ru	0.5% K	γ -alumina	Ru- and K-Promoted Base Catalyst similar to Co.028 but 30% Co	P

Table 2. Summary of Analytical Results

Catalyst	Co	Re	Ru
Co.001	16.6	1.21	--
Co.002	16.1	--	0.37
Co.003	17	--	0.42
Co.005	17.2	--	--
Co.008	15.8	--	--
Co.011	17.2	--	--
Co.012	17.2	--	--
Co.015	17	--	0.29
Co.016	16.7	--	0.31
Co.017	16.6	--	0.31
Co.018	17	--	0.29

Table 3. Summary of Physical Properties

CATALYST	Composition	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Dia. (Å)	Average Part. Size (μm)
Vista-B Al ₂ O ₃	(0-400 mesh)	299	1.69	269	24.50
Vista-B Al ₂ O ₃	Calcined 500°C	240	0.49	82	
Vista-B Al ₂ O ₃	Calcined 600°C	206	0.49	95	
Vista-B Al ₂ O ₃	Calcined 600°C	174	0.47	109	
Davison SiO ₂	(0-400 mesh)	219	0.51	89	121.22
Degussa P25 TiO ₂	(as received)	47	0.40	335	6.08
Co.001	20Co/1Re/ 1La ₂ O ₃ /0.13K/A	191	0.31	66	42.02 40.01
Co.002	20Co/0.43Ru/ 1La ₂ O ₃ /A	149	0.33	89	73.61
Co.003	20Co/0.5Ru/ 1La ₂ O ₃ /A	122	0.26	87	76.81
Co.004	20Co/0.43Ru/ 1La ₂ O ₃ /A				
Co.005	20Co/A	173	0.34	81	64.53 85.66
Co.006	20Co/0.75Re/T				
Co.007	20Co/T				
Co.008	20Co/S	181	1.06	234	
Co.009	20Co/0.5/A				
Co.010	20Co/A				
Co.011	20Co/S	191			
Co.012	20Co/S	211			
Co.013	20Co/T				
Co.014	20Co/0.5Ru/T				
Co.015	20Co/0.43Ru/ 1La ₂ O ₃ /A	141			67.41
Co.016	20CoB/0.43Ru/ 1La ₂ O ₃ /A	116			78.79
Co.017	20Co/0.5Ru/ 1La ₂ O ₃ /A	123			72.80
Co.018	20Co/0.5Ru/A	158			69.48
Co.019	20Co/0.5Ru/S				110.13

Table 4. XRD of Cobalt Catalysts

Catalyst	Catalyst Crystal Phases			
	Calcined	Reduced	After CO Reaction	Co ₃ O ₄ dp (nm)
Co.001	Co ₃ O ₄ γAl ₂ O ₃	Co ₃ O ₄ , Co, Co ₂ O ₃ γAl ₂ O ₃ , CoO	Co ₃ O ₄ γAl ₂ O ₃ , Co	26
Co.002	Co ₃ O ₄ , γAl ₂ O ₃	Co ₃ O ₄ , Co, Co ₂ O ₃ γAl ₂ O ₃ , CoO	Co ₃ O ₄ , Co ₂ O ₃ γAl ₂ O ₃ , Co	19
Co.003			Co ₃ O ₄ , Co γAl ₂ O ₃ , CoO	
Co.005	Co ₃ O ₄ γAl ₂ O ₃	Co ₃ O ₄ , Co γAl ₂ O ₃ , CoO	Co ₃ O ₄ γAl ₂ O ₃ , Co	20
Co.008	Co ₃ O ₄	Co ₃ O ₄ Co		32
Co.011	Co ₃ O ₄	Co ₃ O ₄ Co, Co ₂ O ₃		27
Co.012	Co ₃ O ₄	Co ₃ O ₄ Co, Co ₂ O ₃	Co ₃ O ₄ , Co ₂ O ₃ , Co	24
Co.015	Co ₃ O ₄ γAl ₂ O ₃			16.4
Co.016	Co ₃ O ₄ γAl ₂ O ₃			20
Co.017	Co ₃ O ₄ γAl ₂ O ₃			15.5
Co.018	Co ₃ O ₄			23
Co.019	Co ₃ O ₄			23

Table 5. H₂ Chemisorption^a on the Cobalt Catalysts

Catalyst	Total H ₂ (μ mol/g cat)	Irreversible H ₂ (μ mol/g cat)	Average d _p ^{b,c} (nm)	Dispersion (%)
Co.001	174 $\pm$ 5	157 $\pm$ 5	9.75 $\pm$ 0.25	10.25 $\pm$ 0.25
Co.002	155	130	11	9.1
Co.003	165	140	10.5	9.6
Co.005	48	42	35	2.8
Co.011	82	70	20.8	4.8
Co.012	89	74	19.2	5.2
Co.015	146	124	11.7	8.6
Co.016	163	146	10.5	9.6
Co.017	202	183	8.5	11.9
Co.018	185	165	9.2	11
Co.019	112	92	15	6.6
Co.021	74	24	23	4.3
Co.022	141	122	12	8.3
Co.023	158	136	10.8	9.3

(a) Static H₂ chemisorption at 100°C.

(b) Est. assuming H_{tot}/Co_s = 1

(c) 5.46×10^{-20} m²/Co_s and d_p = 5/S_{Co}/ρ

Table 6. Summary of Fixed Bed Reaction Results

Catalyst	Run	% CO Conv.	Rate g CH ₂ / g cat/hr	wt% CH ₄	alpha	C3-C5 Ole/Par	wt% CO ₂	E act. kcal/ mol	order H ₂ CO	Time on Stream	Startup
Co.001	2	6.1	0.206	25.9	0.66			21.5		51.3 hrs	old
"	3	5.3	0.176	23.3	0.65	3.80		33.4		24.5 hrs	old
Co.002	1	23.2	0.865	84.0	0.47	1.13		8.0		47.3 hrs	old
"	2	33.1	1.851	92.9	0.43	1.77				22.4 hrs	old
"	3	1.4	0.159	29.3	0.49	2.07				22.0 hrs	slow CO
"	4	6.7	0.258	26.1	0.64	1.97	0.030			25.5 hrs	new
Co.003	1	5.5	0.185	30.8	0.57	4.22		28.9		40.0 hrs	old
Co.004											
Co.005	1	10.0	0.168	33.3	0.59	2.52		26.8		23.6 hrs	old
"	2	3.3	0.087	21.4	0.66	3.40	0.017			30.7 hrs	new
"	2a	2.5	0.066	25.9	0.59	4.92	0.010			56.7 hrs	new
"	2b	2.4	0.064	26.3	0.60	6.22	0.012			54.7 hrs	new
Co.006											
Co.007											
Co.008											
Co.009											
Co.010											
Co.011	1	2.5	0.054	25.8	0.62	4.10		21.9		25.5 hrs	slow CO
Co.012	1	3.8	0.083	26.3	0.64	4.40		22.5		22.0 hrs	slow CO
Co.013											
Co.014											
Co.015	1	6.8	0.211	26.7	0.60	3.30				24.0 hrs	slow CO
Co.016	1	5.2	0.161	33.6	0.56	6.85				27.0 hrs	slow CO
Co.017	1	13.2	0.381	77.6	0.61	9.85				29.0 hrs	slow CO
"	2	4.6	0.139	22.0	0.69	3.72	0.039			24.5 hrs	new
"	2a	3.7	0.111	25.9	0.64	4.19	0.021			28.5 hrs	new
"	2b	3.4	0.102	26.9	0.65	4.39	0.024			34.5 hrs	new
Co.018	1	8.6	0.263	32.6	0.62	1.77		23.5		27.0 hrs	slow CO
"	2	3.4	0.170	27.2	0.69	2.24	0.026			25.0 hrs	new
Co.019	1	4.4	0.088	15.2	0.74	7.61				25.9 hrs	new
Co.020											

all reactions are compared at 220°C, H₂:CO = 2:1, and atmospheric pressure

run # 2a indicates the addition of Ar to the reactant feed

run # 2b indicates the addition of Ar saturated with water at 35°C

APPENDIX A

Co Catalyst Formulations

Catalyst Prep:	Co.026	Date	Sep-03-93	Amount	200.0 g
Component		wt		SiO ₂	
(%wt)		20			

Support	Silica Davison Grade 59	Amount	160.00 g
Particle Size	400 -250 mesh	Treatment	500°C / 10 hr
Cobalt	Cobalt Nitrate	Amount	197.29 g
Metal		Amount	
Precursor		Amount	
Precursor		Amount	
Precursor		Amount	

PROCEDURE

Preparation	X	Incipient Wetness	Wet Impregnation
		Ion Exchange	Other
Notes	Incipient wetness: aqueous solution - ca. 1.2 ml/g support Dry catalyst precursor in an oven at 115°C / 5 hr		
Calcination	Temperature	/	Time /
Notes			

Co.026: 20 wt% Co
 SiO₂

Non-promoted catalyst similar to Co.012 using different silica grade (Davison Grade 59).

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.

Catalyst Prep	Co.027	Date Tech	Sep-03-93	Amount	200.0 g
Compound (%wt)	Co	Ru	SiO ₂		
	20	0.5			

Support	Silica Davison Grade 59	Amount	159.00 g
Particle Size	400 - 250 mesh	Treatment	500°C / 10 hrs
Catalyst	Cobalt Nitrate	Amount	197.29 g
Metal	Ruthenium Nitrosyl nitrate	Amount	3.73 g
Promoter		Amount	
Promoter		Amount	
Promoter		Amount	

PROCEDURE

Preparation	X	Incipient Wetness Ion Exchange	Wet Impregnation Other
Notes	Incipient wetness: aqueous solution - ca. 1.2 ml/g Dry catalyst precursor in an oven at 115°C / 5 hrs, moderate stirring		
Calcination	Temperature	/	Time /
Notes			

Co.027: 20 wt% Co
 0.5 wt% Ru
 SiO₂

Ru-promoted catalyst similar to Co.019 using different silica grade (Davison Grade 59).

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], and Ru nitrosyl nitrate 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.**

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.028: 20 wt% Co
 0.5 wt% Ru
 0.5 wt% K
 γ -alumina

Ru/K-promoted catalyst similar otherwise to the Re + La-promoted STATOIL catalyst based heavily 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 [Co(NO₃)₂·6H₂O] and Ru nitrosil nitrate and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

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

The dried catalyst is then calcined in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

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.029: 30 wt% Co
 0.5 wt% Ru
 0.5 wt% K
 γ -alumina

Ru/K-promoted catalyst similar otherwise to the Re + La-promoted STATOIL catalyst based heavily 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 in 2 steps with an aqueous solution of Co nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, Ru nitrosyl nitrate, and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with 60% of the desired loading of Co, Ru, and K in the first step. Dry in air at 115°C for 12 hours and calcine in air at 300°C for 2 hours (heating rate of ca. 1°C/min to 300°C). In the second step, impregnate the remaining 40% of the Co, Ru, and K. Repeat the drying and calcination procedures. Impregnate the support with an aqueous solution of Co nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and Ru nitrosyl nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co.

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.020c: 20 wt% Co
 0.4 wt% Ru
 γ -alumina

Ru/Co catalyst prepared from **precalcined** Ru base catalyst Co.020.

Preparation Procedure:

Impregnate the **precalcined catalyst precursor** (Co.020) 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.

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.

APPENDIX B

Characterization Data

TPR Pattern for Co.002(p,c,r)

TPR Pattern for Co.002(p,c,r,sbr)

XRD Pattern for Co.003 (p,c,r,sbr)

XRD Pattern for Co.011 (p,c)

XRD Pattern for Co.011 (p,c,r,sbr)

XRD Pattern for Co.012 (p,c)

XRD Pattern for Co.012 (p,c,r)

XRD Pattern for Co.012 (p,c,r,sbr)

XRD Pattern for Co.015 (p,c)

XRD Pattern for Co.016 (p.c)

XRD Pattern for Co.017 (p,c)

XRD Pattern for Co.018 (p,c)

XRD Patterns of As Received TiO₂

XRD Patterns of TiO_2 Calcined at 650°C for 16 Hours

XRD Patterns of TiO_2 Calcined at 650 °C for 24 Hours

XRD Patterns of Wet TiO_2 Calcined at 650 °C for 16 Hours

XRD Patterns of Wet TiO_2 Calcined at 650 °C for 24 Hours

**XRD Patterns of TiO_2 (wetted and dried at 60°C)
Calcined at 650°C for 16 Hours**

**XRD Patterns of TiO_2 (wetted and dried at 60°C)
Calcined at 700°C for 16 Hours**

XRD Patterns of TiO_2 Calcined at 750 °C for 24 Hours

XRD Patterns of TiO_2 Calcined at 750°C for 18 Hours

**XRD Patterns of TiO_2 (wetted and dried at 60°C)
Calcined at 750°C for 16 Hours**

XRD Patterns of As Received TiO_2 and Calcined TiO_2 ,
750°C (50/50 by wt.)

XRD Patterns of TiO_2 Calcined at 900°C for 24 Hours

XRD Patterns of Vista B (0-400) Calcined at 500 °C for 10
Hours

XRD Patterns of Vista B (0-400) Calcined at 600 °C for 5 Hours

XRD Patterns of Vista B (0-400) Calcined at 750 °C for 16 Hours

Static H₂ Chemisorption at 100 °C Isotherms for Co.003 (p,c,fr)

Static H₂ Chemisorption at 100 °C Isotherms for Co.005 (p,c,fr)

Static H₂ Chemisorption at 100 °C Isotherms for Co.011 (p,c,fr)

Static H₂ Chemisorption at 100 °C Isotherms for Co.012 (p,c,fr)

Static H_2 Chemisorption at 100 °C Isotherms for Co.015 (p,c,fr)

Static H₂ Chemisorption Isotherms for Co.016(p,c,r)

Static H₂ Chemisorption at 100 °C Isotherms for Co.017 (p,c,fr)

Static H₂ Chemisorption at 100 °C Isotherms for Co.018 (p,c,fr)

Static H₂ Chemisorption at 100 °C Isotherms for Co.019 (p,c,fr)

Static H₂ Chemisorption at 100 °C of Co.021

Static H₂ Chemisorption at 100°C of Co.022

Static H_2 Chemisorption at 100 °C of Co.023

APPENDIX C

Fixed Bed Reaction Data

Co.002 - Run #3

Co wt%	NM wt%	Promotor wt%		Support
20	Ru 0.43		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 2.07

weight of catalyst = 0.06 g

WHSV = 25.57 1/hr

time on stream = 22.0 hrs

CO conversion (%)	1.4
rate (g CH ₂ /g cat/hr)	0.16
alpha	0.49
C1 (wt%)	29.3
C2 - C4 (wt%)	34.8
C5 - C12 (wt%)	35.7
C13 + (wt%)	0.3

Performance of Co.002

Run #3

flow rate = 50.0 cc/min, loading = 0.1 g, WHSV = 25.6 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	2.0	5.0	22.0
reaction temperature, °C	220	220	220
pressure, atm	1	1	1

C1 - C15 product distribution, weight %			
C1	23.70	25.64	29.51
C2	5.53	5.87	6.48
C3	12.53	12.95	13.87
C4	14.58	14.64	14.80
C5	14.56	14.82	13.47
corr	14.02	12.98	11.99
C7	8.59	7.01	5.85
C8	4.03	3.81	2.61
C9	2.45	2.29	1.42
C10			
C11			
C12			
C13			
C14			
C15			
alpha chain growth probability	0.55	0.54	0.49

C1 - C50 estimated total product distribution, weight %			
C1	23.2	25.1	29.3
C2 - C4	31.9	32.8	34.8
C5 - C12	44.1	41.4	35.7
C13 - C50	0.8	0.7	0.3

CO conversion, %	1.7	1.6	1.4
rate, g CH ₂ /g cat/hr	0.19	0.18	0.16

Co.002 - Run #4

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.43		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.16 g

WHSV = 8.82 1/hr

time on stream = 25.5 hrs

CO₂ (%) = 0.030

O/P = 1.97

CO conversion (%)	6.7
rate (g CH ₂ /g cat/hr)	0.26
alpha	0.64
C1 (wt%)	26.1
C2 - C4 (wt%)	31.9
C5 - C12 (wt%)	39.5
C13 + (wt%)	2.6

Co.002 - Run #4

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.43		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm	CO ₂ (%) = 0.030
T = 220 °C	O/P = 1.97
H ₂ /CO = 2	
weight of catalyst = 0.16 g	
WHSV = 8.82 1/hr	
time on stream = 25.5 hrs	

CO conversion (%)	6.7
rate (g CH ₂ /g cat/hr)	0.26
alpha	0.64
C1 (wt%)	26.1
C2 - C4 (wt%)	31.9
C5 - C12 (wt%)	39.5
C13 + (wt%)	2.6

Performance of Co.002

Run #4

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 8.8 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	3.0	7.5	19.3	21.5	23.8	25.5
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1
C1 - C15 product distribution, weight %						
C1	23.24	23.29	24.96	25.93	25.98	26.26
C2	4.69	4.61	4.81	4.99	4.99	5.05
C3	13.46	13.00	13.00	13.43	13.42	13.49
C4	14.22	13.69	13.20	13.58	13.54	13.52
C5	12.26	11.84	12.14	11.51	11.52	11.47
C6	9.05	8.46	8.09	8.37	8.34	8.15
C7	6.64	7.09	7.09	6.64	6.74	6.64
C8	4.74	5.12	5.05	4.81	4.80	4.75
C9	3.41	3.71	3.65	3.36	3.42	3.40
C10	2.52	2.73	2.61	2.49	2.49	2.46
C11	1.69	2.14	1.72	1.58	1.59	1.57
C12	1.23	1.44	1.28	1.17	1.06	1.07
C13	0.82	0.83	0.73	0.66	0.68	0.67
C14	0.63	0.62	0.54	0.49	0.49	0.50
C15	0.42	0.44	0.36	0.32	0.32	0.32
alpha chain growth probability	0.66	0.66	0.64	0.63	0.64	0.64
C1 - C50 estimated total product distribution, weight %						
C1	23.0	23.2	25.0	26.0	25.9	26.1
C2 - C4	32.0	31.2	31.0	32.0	31.9	31.9
C5 - C12	41.6	42.2	41.4	39.8	39.9	39.5
C13 - C50	3.4	3.4	2.5	2.2	2.4	2.6
CO conversion, %	7.7	7.1	7.4	7.1	6.9	6.7
rate, g CH ₂ /g cat/hr	0.30	0.27	0.28	0.27	0.27	0.26

Schulz-Flory Plot for Co.002 - Run #4
Time on Stream (hrs)

Co.005 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
20				Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.24 g

WHSV = 6.00 1/hr

time on stream = 30.7 hrs

CO₂ (%) = 0.017

O/P = 3.40

CO conversion (%)	3.3
rate (g CH ₂ /g cat/hr)	0.09
alpha	0.66
C1 (wt%)	21.4
C2 - C4 (wt%)	24.4
C5 - C12 (wt%)	49.9
C13 + (wt%)	4.3

Performance of Co.005

Run #2

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 6.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	3.3	6.0	11.7	21.8	25.0	30.7
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1

C1 - C15 product distribution, weight %						
C1	20.76	20.63	20.79	23.05	21.84	21.87
C2	3.67	3.64	3.58	3.69	3.56	3.53
C3	10.52	10.26	10.01	10.09	9.90	9.61
C4	12.84	12.40	12.26	12.33	12.04	11.74
C5	14.66	14.34	14.12	14.05	13.83	13.58
C6	12.30	11.98	12.47	12.24	12.29	12.82
C7	7.36	7.57	7.63	7.38	7.73	7.63
C8	5.19	5.38	5.41	5.22	5.49	5.53
C9	3.72	3.91	3.98	3.68	3.97	4.06
C10	2.58	2.88	2.85	2.58	2.90	2.98
C11	1.88	2.04	2.00	1.79	1.90	1.94
C12	1.47	1.42	1.34	1.43	1.29	1.37
C13	1.11	1.11	1.02	0.90	0.95	0.99
C14	0.80	0.84	0.78	0.64	0.72	0.74
C15	0.56	0.64	0.59	0.49	0.55	0.54
alpha chain growth probability	0.64	0.66	0.66	0.65	0.66	0.66

C1 - C50 estimated total product distribution, weight %						
C1	20.5	20.2	20.3	22.6	21.3	21.4
C2 - C4	26.7	25.7	25.3	25.6	24.8	24.4
C5 - C12	49.2	49.5	49.9	48.1	49.4	49.9
C13 - C50	3.5	4.6	4.5	3.6	4.5	4.3

CO conversion, %	3.7	3.7	3.8	3.3	3.5	3.3
rate, g CH ₂ /g cat/hr	0.10	0.10	0.10	0.09	0.09	0.09
CO ₂ formation, %	0.017	0.017	0.018	0.016	0.018	0.017

Schulz-Flory Plot for Co.005 - Run #2
Time on Stream (hrs)

Performance of Co.005

Run #2 Exp. #2

flow rate = 85.5 cc/min, loading = 0.2 g, WHSV = 22.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	32.2	48.7	50.7	52.7	54.7	56.7
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1
	+Ar	+Ar	+H ₂ O	+H ₂ O	+H ₂ O	+Ar

C1 - C15 product distribution, weight %

C1	26.01	26.78	26.09	26.78	26.25	25.80
C2	4.44	4.44	4.30	4.35	4.29	4.31
C3	11.85	11.96	11.61	11.74	11.60	11.62
C4	13.25	13.39	13.05	11.75	11.73	13.16
C5	14.03	14.51	14.02	14.05	13.60	14.04
C6	13.30	13.30	13.17	13.06	14.64	13.18
C7	6.49	6.15	6.66	6.78	6.69	6.60
C8	4.22	3.84	4.38	4.43	4.30	4.16
C9	2.54	2.22	2.68	2.86	2.60	2.56
C10	1.62	1.34	1.63	1.72	1.78	1.86
C11	0.91	0.84	0.99	0.96	0.98	1.01
C12	0.46	0.53	0.57	0.57	0.57	0.57
C13	0.43	0.38	0.45	0.40	0.42	0.43
C14	0.16	0.19	0.24	0.26	0.30	0.33
C15	0.12	0.09	0.01	0.12	0.11	0.20
alpha chain growth probability	0.57	0.58	0.59	0.60	0.60	0.59

C1 - C50 estimated total product distribution, weight %

C1	26.1	26.7	26.1	26.8	26.3	25.9
C2 - C4	29.6	29.7	28.9	27.8	27.6	29.2
C5 - C12	43.5	42.7	44.0	44.4	45.1	44.0
C13 - C50	0.7	0.9	1.0	1.0	1.0	1.0

CO conversion, %	2.7	2.5	2.4	2.4	2.4	2.5
rate, g CH ₂ /g cat/hr	0.07	0.07	0.06	0.06	0.06	0.07
CO ₂ formation, %	0.009	0.010	0.013	0.013	0.012	0.010

Schulz-Flory Plot for Co.005 - Run #2 Exp #2
Time on Stream (hrs)
hollow symbols indicate water addition

Co.015 - Run #1

Co wt%	NM wt%	Promotor wt%		Support
20	Ru 0.43		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 3.30

weight of catalyst = 0.20 g

WHSV = 7.08 1/hr

time on stream = 24.0 hrs

CO conversion (%)	6.8
rate (g CH ₂ /g cat/hr)	0.21
alpha	0.67
C1 (wt%)	26.7
C2 - C4 (wt%)	31.9
C5 - C12 (wt%)	40.2
C13 + (wt%)	1.2

Performance of Co.015

Run #1

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 7.1 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	3.0	5.0	8.0	24.0
reaction temperature, °C	220	220	220	220
pressure, atm	1	1	1	1
C1 - C15 product distribution, weight %				
C1	24.90	23.44	24.07	26.93
C2	4.89	4.63	4.72	5.16
C3	14.76	13.39	13.24	13.44
C4	17.05	14.14	13.88	13.60
C5	11.28	13.56	13.21	13.00
C6	20.57	11.52	11.07	11.34
C7	3.51	7.43	7.42	6.69
C8	1.90	4.57	4.95	4.02
C9	0.81	2.87	2.87	2.42
C10	0.25	1.79	1.81	1.44
C11	0.09	1.22	1.25	0.99
C12		0.86	0.90	0.68
C13		0.59	0.61	0.30
C14				
C15				
alpha chain growth probability	0.49	0.61	0.62	0.60
C1 - C50 estimated total product distribution, weight %				
C1	24.8	23.2	23.8	26.7
C2 - C4	36.5	31.8	31.5	31.9
C5 - C12	38.6	43.4	43.0	40.2
C13 - C50	0.2	1.7	1.8	1.2
CO conversion, %	7.1	8.0	7.8	6.8
rate, g CH ₂ /g cat/hr	0.22	0.25	0.24	0.21

Schulz-Flory Plot for Co.015 - Run #1
Time on Stream (hrs)

Co.016 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.43		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 6.85

weight of catalyst = 0.20 g

WHSV = 7.05 1/hr

time on stream = 27.0 hrs

CO conversion (%)	5.2
rate (g CH ₂ /g cat/hr)	0.16
alpha	0.56
C1 (wt%)	33.6
C2 - C4 (wt%)	34.4
C5 - C12 (wt%)	31.3
C13 + (wt%)	0.6

Performance of Co.016

Run #1

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 7.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	11.8	24.5	27.0	28.8
reaction temperature, °C	220	220	220	220
pressure, atm	1	1	1	1

C1 - C15 product distribution, weight %

C1	30.56	34.61	33.79	34.25
C2	6.04	6.83	6.65	6.74
C3	14.24	15.26	14.75	14.87
C4	13.31	13.55	13.17	13.22
C5	11.77	11.54	11.34	11.36
C6	11.74	8.85	9.83	9.00
C7	5.30	4.20	4.49	4.50
C8	2.92	2.47	2.63	2.65
C9	1.60	1.28	1.41	1.38
C10	0.93	0.70	0.76	0.73
C11	0.59	0.35	0.42	0.50
C12	0.37	0.23	0.30	0.31
C13	0.27	0.13	0.21	0.21
C14	0.20		0.14	0.16
C15	0.16		0.12	0.12
alpha chain growth probability	0.58	0.52	0.56	0.57

C1 - C50 estimated total product distribution, weight %

C1	30.4	34.5	33.6	34.1
C2 - C4	33.4	35.6	34.4	34.7
C5 - C12	35.4	29.6	31.3	30.6
C13 - C50	0.8	0.3	0.6	0.7

CO conversion, %	4.9	5.0	5.2	4.9
rate, g CH ₂ /g cat/hr	0.15	0.16	0.16	0.15

Schulz-Flory Plot for Co.016 - Run #1
Time on Stream (hrs)

Co.017 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 9.85

weight of catalyst = 0.22 g

WHSV = 6.59 1/hr

time on stream = 29.0 hrs

CO conversion (%)	13.2
rate (g CH ₂ /g cat/hr)	0.38
alpha	0.61
C1 (wt%)	77.6
C2 - C4 (wt%)	10.8
C5 - C12 (wt%)	11.1
C13 + (wt%)	0.4

Performance of Co.017

Run #1

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 6.6 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	2.5	5.0	8.0	24.0	26.5	29.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1
C1 - C15 product distribution, weight %						
C1	66.91	72.45	74.54	78.44	79.43	77.68
C2	3.44	2.75	2.46	2.47	2.17	2.37
C3	7.37	5.74	5.05	4.81	4.21	4.55
C4	6.12	4.88	4.39	4.14	3.64	3.93
C5	5.31	4.37	4.01	3.79	3.37	3.60
C6	3.51	3.28	3.49	2.77	2.45	2.64
C7	2.63	2.31	2.16	1.53	1.77	1.92
C8	1.68	1.48	1.35	0.86	1.09	1.22
C9	1.06	0.94	0.86	0.48	0.66	0.74
C10	0.70	0.61	0.56	0.29	0.40	0.43
C11	0.43	0.39	0.39	0.18	0.25	0.27
C12	0.27	0.23	0.21	0.12	0.16	0.18
C13	0.19	0.17	0.16	0.07	0.12	0.14
C14	0.14	0.13	0.13	0.04	0.10	0.11
C15	0.11	0.11	0.09	0.02	0.09	0.11
alpha chain growth probability	0.54	0.60	0.63	0.55	0.62	0.61
C1 - C50 estimated total product distribution, weight %						
C1	67.4	72.6	74.3	78.4	79.2	77.6
C2 - C4	17.0	13.4	11.9	11.4	10.0	10.8
C5 - C12	15.4	13.6	13.2	10.0	10.3	11.1
C13 - C50	0.2	0.4	0.7	0.1	0.5	0.4
CO conversion, %	19.3	16.8	15.8	13.3	11.6	13.2
rate, g CH ₂ /g cat/hr	0.56	0.48	0.45	0.38	0.33	0.38

Schulz-Flory Plot for Co.017 - Run #1
Time on Stream (hrs)

Co.017 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50		La2O3 1.00	Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.21 g

WHSV = 6.93 1/hr

time on stream = 24.5 hrs

CO₂ (%) = 0.039

O/P = 3.72

CO conversion (%)	4.6
rate (g CH ₂ /g cat/hr)	0.14
alpha	0.69
C1 (wt%)	22.0
C2 - C4 (wt%)	20.6
C5 - C12 (wt%)	51.6
C13 + (wt%)	5.8

Performance of Co.017

Run #2

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 6.9 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	4.0	7.0	22.3	24.5
reaction temperature, °C	220	220	220	220
pressure, atm	1	1	1	1

C1 - C15 product distribution, weight %				
C1	19.55	19.14	21.70	21.48
C2	3.13	3.05	3.18	3.14
C3	8.10	7.74	7.93	7.82
C4	9.99	9.30	9.42	9.17
C5	12.15	11.46	11.29	11.13
C6	11.42	11.68	10.81	12.13
C7	8.17	8.00	7.82	7.63
C8	6.44	6.45	6.15	6.06
C9	5.02	5.05	4.83	4.81
C10	4.00	5.41	4.18	4.08
C11	3.13	5.19	3.37	3.25
C12	2.42	2.44	2.54	2.57
C13	1.78	1.93	1.77	1.84
C14	1.36	1.08	1.22	1.23
C15	1.03	0.76	0.85	0.82
alpha chain growth probability	0.70	0.69	0.69	0.69

C1 - C50 estimated total product distribution, weight %				
C1	19.4	19.7	22.2	22.0
C2 - C4	21.1	20.6	21.0	20.6
C5 - C12	52.4	54.1	50.9	51.6
C13 - C50	7.1	5.6	6.0	5.8

CO conversion, %	6.2	5.9	4.7	4.6
rate, g CH ₂ /g cat/hr	0.19	0.18	0.14	0.14
CO ₂ formation, %	0.053	0.050	0.040	0.039

Schulz-Flory Plot for Co.017 - Run #2
Time on Stream (hrs)

Performance of Co.017

Run #2 Exp. #2

flow rate = 85.0 cc/min, loading = 0.2 g, WHSV = 6.9 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	26.5	28.5	34.5	45.0	47.0	49.0
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1
	+Ar	+Ar	+H ₂ O	+Ar	+Ar	no Ar
C1 - C15 product distribution, weight %						
C1	25.81	25.86	26.92	27.74	27.68	23.29
C2	3.85	3.89	3.88	3.99	3.95	3.24
C3	9.57	9.57	9.53	9.79	9.74	8.06
C4	10.48	10.52	10.52	10.63	10.60	9.54
C5	11.98	11.90	11.83	12.18	11.92	11.42
C6	11.78	11.75	11.44	11.66	11.51	10.98
C7	7.38	7.32	7.25	7.43	7.20	7.69
C8	5.39	5.35	5.28	5.11	5.13	5.96
C9	3.97	3.88	3.81	3.54	3.64	4.68
C10	2.93	2.92	2.85	2.64	2.70	3.90
C11	2.07	2.16	1.92	1.69	1.84	3.15
C12	1.47	1.44	1.44	1.17	1.29	2.33
C13	0.92	1.03	0.99	0.76	0.85	1.61
C14	0.58	0.63	0.67	0.51	0.52	1.13
C15	0.43	0.40	0.50	0.34	0.35	0.71
alpha chain growth probability	0.64	0.64	0.65	0.63	0.63	0.68
C1 - C50 estimated total product distribution, weight %						
C1	26.0	26.2	26.9	27.8	27.9	23.8
C2 - C4	24.1	24.3	23.9	24.5	24.5	21.3
C5 - C12	47.0	46.8	45.9	45.4	45.2	50.0
C13 - C50	2.9	2.7	3.3	2.3	2.4	4.9
CO conversion, %	3.7	3.7	3.4	3.2	3.2	3.7
rate, g CH ₂ /g cat/hr	0.11	0.11	0.10	0.10	0.10	0.11
CO ₂ formation, %	0.018	0.021	0.024	0.020	0.020	0.035

Schulz-Flory Plot for Co.017 - Run #2 Exp #2
Time on Stream (hrs)
Hollow Symbols Represent Addition of Water

Co.018 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al ₂ O ₃

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 1.77

weight of catalyst = 0.21 g

WHSV = 6.95 1/hr

time on stream = 27.0 hrs

E_a = 23.5 kcal/mol

CO conversion (%)	8.6
rate (g CH ₂ /g cat/hr)	0.26
alpha	0.62
C1 (wt%)	32.6
C2 - C4 (wt%)	30.9
C5 - C12 (wt%)	34.9
C13 + (wt%)	1.6

Performance of Co.018

Run #1

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 7.0 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	2.0	5.0	8.0	24.2	27.0	29.0
reaction temperature, °C	220	220	220	220	220	210
pressure, atm	1	1	1	1	1	1

C1 - C15 product distribution, weight %

C1	89.26	29.97	29.06	33.13	32.62	25.40
C2	6.85	5.13	4.88	5.38	5.29	4.25
C3	2.17	13.50	12.77	13.68	13.41	11.47
C4	0.98	13.10	12.15	12.56	12.22	11.65
C5	0.54	11.60	12.48	11.17	10.88	11.48
C6	0.10	8.37	7.89	8.24	7.76	8.89
C7	0.06	6.31	7.16	5.81	6.25	7.91
C8	0.03	4.02	4.56	3.58	3.93	5.38
C9	0.01	2.58	2.92	2.31	2.51	3.77
C10		1.68	1.96	1.48	1.62	2.65
C11		1.21	1.32	0.95	1.15	1.90
C12		0.81	0.88	0.63	0.75	1.52
C13		0.58	0.66	0.42	0.54	1.12
C14		0.41	0.45	0.30	0.37	0.86
C15		0.32	0.35	0.23	0.30	0.70
alpha chain growth probability	0.32	0.62	0.63	0.62	0.62	0.70

C1 - C50 estimated total product distribution, weight %

C1	89.3	30.0	29.0	32.9	32.6	24.7
C2 - C4	10.0	31.8	29.8	31.4	30.9	26.6
C5 - C12	0.7	36.6	39.2	34.2	34.9	43.3
C13 - C50	0.0	1.6	2.0	1.5	1.6	5.5

CO conversion, %	18.9	10.3	10.0	8.7	8.6	5.5
rate, g CH ₂ /g cat/hr	0.57	0.31	0.31	0.27	0.26	0.17

Performance of Co.018

Run #1

flow rate = 50.0 cc/min, loading = 0.2 g, WHSV = 7.0 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	30.5	32.3
reaction temperature, °C	230	220
pressure, atm	1	1

C1 - C15 product distribution, weight %

C1	40.36	31.57
C2	6.07	5.10
C3	13.91	13.19
C4	11.67	12.07
C5	9.46	10.83
C6	6.98	8.03
C7	4.65	6.57
C8	2.73	4.21
C9	1.65	2.71
C10	0.99	1.94
C11	0.55	1.20
C12	0.33	0.82
C13	0.22	0.57
C14	0.16	0.43
C15	0.12	0.32
alpha chain growth probability	0.55	0.60

C1 - C50 estimated total product distribution, weight %

C1	40.5	32.0
C2 - C4	31.8	30.8
C5 - C12	27.3	36.2
C13 - C50	0.4	1.1

CO conversion, %	14.0	7.8
rate, g CH ₂ /g cat/hr	0.43	0.24

Co.018 Arrhenius Plot - Run #1

Schulz-Flory Plot for Co.018 - Run #1
Time on Stream (hrs)

Schulz-Flory Plot for Co.018 - Run #1
Alpha as a Function of Temperature

Co.018 - Run #2

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			Al2O3

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

weight of catalyst = 0.13 g

WHSV = 11.34 1/hr

time on stream = 25.0 hrs

CO₂ (%) = 0.026

O/P = 2.24

CO conversion (%)	3.4
rate (g CH ₂ /g cat/hr)	0.17
alpha	0.69
C1 (wt%)	27.2
C2 - C4 (wt%)	22.9
C5 - C12 (wt%)	45.5
C13 + (wt%)	4.5

Performance of Co.018

Run #2

flow rate = 50.0 cc/min, loading= 0.1 g, WHSV = 11.3 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	4.0	9.5	23.0	25.0
reaction temperature, °C	220	220	220	220
pressure, atm	1	1	1	1

C1 - C15 product distribution, weight %

C1	24.51	25.95	27.10	27.23
C2	3.58	3.65	3.71	3.71
C3	9.23	9.12	8.99	8.95
C4	10.76	10.54	10.28	10.26
C5	12.30	11.96	11.65	11.62
C6	11.26	10.95	10.81	10.93
C7	7.34	7.19	7.07	7.02
C8	5.48	5.44	5.36	5.26
C9	4.02	4.01	3.95	3.96
C10	3.14	3.12	3.05	3.06
C11	2.23	2.20	2.25	2.30
C12	1.67	1.70	1.69	1.68
C13	1.21	1.12	1.18	1.18
C14	0.85	0.85	0.82	0.84
C15	0.65	0.63	0.56	0.53
alpha chain growth probability	0.70	0.70	0.69	0.69

C1 - C50 estimated total product distribution, weight %

C1	24.1	25.7	27.1	27.2
C2 - C4	23.2	23.1	22.9	22.9
C5 - C12	47.1	46.2	45.5	45.5
C13 - C50	5.6	5.0	4.5	4.5

CO conversion, %	4.2	3.9	3.5	3.4
rate, g CH ₂ /g cat/hr	0.21	0.19	0.17	0.17
CO ₂ formation, %	0.026	0.021	0.027	0.026

Schulz-Flory Plot for Co.018 - Run #2
Time on Stream (hrs)

Co.019 - Run #1

Co wt%	NM wt %	Promotor wt%		Support
20	Ru 0.50			SiO ₂

SUMMARY REACTION DATA

Reaction Conditions:

P = 1 atm

T = 220 °C

H₂/CO = 2

O/P = 7.61

weight of catalyst = 0.31 g

WHSV = 4.56 1/hr

time on stream = 25.9 hrs

CO conversion (%)	4.4
rate (g CH ₂ /g cat/hr)	0.09
alpha	0.74
C1 (wt%)	15.2
C2 - C4 (wt%)	22.9
C5 - C12 (wt%)	52.0
C13 + (wt%)	9.9

Performance of Co.019

Run #1

flow rate = 50.0 cc/min, loading = 0.3 g, WHSV = 4.6 1/hr, H₂/CO ratio in feed = 2

time on stream, hr	3.0	8.3	20.5	22.5	24.3	25.9
reaction temperature, °C	220	220	220	220	220	220
pressure, atm	1	1	1	1	1	1
C1 - C15 product distribution, weight %						
C1	14.36	14.63	15.59	15.25	15.49	15.16
C2	3.64	3.79	4.16	4.09	4.17	4.11
C3	8.37	8.27	8.87	8.71	8.84	8.74
C4	9.95	9.55	10.06	9.93	10.02	9.96
C5	10.44	9.86	10.19	10.22	10.28	10.28
C6	8.95	10.34	9.05	9.73	9.08	9.11
C7	8.59	8.20	8.19	8.15	8.20	8.21
C8	7.28	7.02	6.97	6.93	6.96	7.08
C9	6.14	6.01	5.93	5.86	5.91	5.95
C10	5.12	5.05	5.00	4.87	4.95	5.21
C11	4.09	4.10	3.93	3.90	3.94	4.16
C12	3.08	3.16	2.96	3.03	3.05	3.17
C13	2.22	2.29	2.29	2.26	2.28	2.26
C14	1.78	1.73	1.46	1.66	1.74	1.69
C15	1.46	1.34	1.14	1.22	1.14	1.07
alpha chain growth probability	0.74	0.74	0.73	0.74	0.74	0.74
C1 - C50 estimated total product distribution, weight %						
C1	14.4	14.8	16.0	15.4	15.5	15.2
C2 - C4	22.1	21.8	23.7	22.9	23.0	22.9
C5 - C12	52.9	53.0	51.9	52.0	51.4	52.0
C13 - C50	10.6	10.4	8.4	9.7	10.2	9.9
CO conversion, %	4.4	5.0	3.4	4.3	3.6	4.4
rate, g CH ₂ /g cat/hr	0.09	0.10	0.07	0.09	0.07	0.09

Performance of Co.019

Run #1

flow rate = 50.0 cc/min, loading = 0.3 g, WHSV = 4.6 l/hr, H₂/CO ratio in feed = 2

time on stream, hr	25.9
reaction temperature, °C	220
pressure, atm	1

C1 - C15 product distribution, weight %

C1	15.16
C2	4.11
C3	8.74
C4	9.96
C5	10.28
C6	9.11
C7	8.21
C8	7.08
C9	5.95
C10	5.21
C11	4.16
C12	3.17
C13	2.26
C14	1.69
C15	1.07

alpha	chain growth probability	0.74
-------	--------------------------	------

C1 - C50 estimated total product distribution, weight %

C1	15.2
C2 - C4	22.9
C5 - C12	52.0
C13 - C50	9.9

CO conversion, %	4.4
rate, g CH ₂ /g cat/hr	0.09

Schulz-Flory Plot for Co.019 - Run #1
Time on Stream (hrs)

APPENDIX D

Slurry Bubble Column Testing Data

APPENDIX D

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APPENDIX D

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Table I

SUMMARY OF M3 SBCR RUN RESULTS

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

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

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 C5+ (kg/kg cat., hr).

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

Run No	Cat. No	Per wt.,g	Time No	Time Start	Temp Stop	Pres C	H2: psi	Synfld CO	Conv. cc/hr	Prod. %	Selectivity Rate	XC4	XC2-C5	XC6+	Alpha GC	Alpha Liq	Olefin C3	Paraf C4	Olefins C5-C18, %	Comments
2	CO.001	16.5	1	162	177	225	450	2.0	20	15.9	0.51	2.3	25.1	72	0.98	0.88	5.00	2.27	25.2	
2	CO.001	16.5	2	202	228	200	450	2.0	20	3.9	0.15	0.0	10.8	89	0.81	0.91	0.00	0.00	21.7	
2	CO.001	16.5	3	254	280	240	450	2.0	20	30.9	0.80	11.7	28.7	58.5	0.87	0.77	2.63	1.64	22.4	
2	CO.001	16.5	4	302	323	225	450	1.2	20	9.9	0.49	0.7	16.2	82.4	0.76	0.90	0.00	7.14	29.4	
2	CO.001	16.5	5	350	372	225	450	2.0	20	15.3	0.46	6.0	25.1	68.4	0.84	0.88	4.00	2.70	23.1	
2	CO.001	16.5	6	398	420	225	300	2.0	20	12.5	0.36	6.1	27.6	65.7	0.79	0.86	4.35	2.86	21.7	
2	CO.001	16.5	7	446	468	240	300	2.0	20	22.9	0.47	16.5	35.9	46.4	0.71	0.79	3.03	1.79	22.4	
2	CO.001	16.5	8	494	516	240	600	2.0	20	29.9	0.78	12.6	27.7	58.9	0.76	0.82	2.63	1.69	22.4	
2	CO.001	16.5	9	517	540	240	600	2.0	0	29.5	0.75	12.0	29.2	57.9	0.76	--	2.50	1.56	22.4	
2	CO.001	16.5	9	541	564	240	600	2.0	0	28.4	0.76	10.4	28.5	60.3	0.77	--	3.03	1.72	--	
2	CO.001	16.5	9	565	588	240	600	2.0	0	27.9	0.71	11.1	29.9	58.1	0.76	--	3.03	1.72	--	
2	CO.001	16.5	9	589	612	240	600	2.0	0	27.0	0.71	10.7	29.1	59.3	0.76	0.82	2.78	2.00	--	
2	CO.001	16.5	10	637	660	240	600	2.0	20	26.4	0.72	11.0	26.6	61.5	0.77	0.83	2.86	1.96	22.4	G.C. Calib
2	CO.001	16.5	11	684	706	225	450	2.0	20	11.6	0.36	5.4	24.5	69.5	0.81	0.87	5.26	3.45	23.8	
3	CO.005	19.5	1	12	36	240	450	2.0	20	33.2	0.84	5.6	25.6	67.8	0.80	0.81	2.04	1.27	23.1	G.C. Calib
3	CO.005	19.5	2	60	84	220	450	2.0	20	15.0	0.45	2.9	15.5	81.4	0.86	0.87	4.55	3.23	21.7	
3	CO.005	19.5	3	108	132	240	450	1.2	20	18.5	0.66	6.9	22.0	70.3	0.81	--	5.88	3.85	26.6	
3	CO.005	19.5	4	156	179	240	450	2.0	20	29.6	0.65	11.5	28.7	58.9	0.76	0.78	2.22	1.39	21.7	
4	CO.002	20.1	1	37	59	240	450	2.0	20	36.1	0.50	22.9	37.5	38.0	0.66	0.77	0.65	0.31	16.8	
4	CO.002	20.1	2	85	106	220	450	2.0	20	16.6	0.46	3.8	19.3	76.5	0.84	0.88	2.44	0.89	--	
4	CO.002	20.1	3	133	149	210	600	1.0	20	5.2	0.25	0.0	11.2	87.9	0.89	0.94	0.00	0.00	--	Power Fail
5	CO.003	15.1	1	15	35	240	450	2.0	20	31.7	0.73	16.7	34.2	47.9	0.71	0.94	1.30	0.60	18.2	G.C. Calib
5	CO.003	15.1	2	61	83	220	450	2.0	20	13.2	0.45	5.1	23.1	71.3	0.82	0.90	4.55	1.89	--	
5	CO.003	15.1	3	88	107	240	450	2.0	20 ¹	28.4	0.73	15.1	27.8	56.0	0.75	--	1.45	0.97	--	
5	CO.003	15.1	4	133	155	240	450	1.0	20	13.1	0.70	4.2	20.7	73.9	0.83	0.88	6.67	3.70	--	
5	CO.003	15.1	5	181	203	240	600	1.0	20	13.4	0.68	3.9	25.3	69.5	0.81	--	5.26	3.45	30.1	
5	CO.003	15.1	6	217	227	240	450	2.0	20	25.4	0.62	14.9	33.1	50.9	0.73	--	1.89	1.19	--	
6	CO.011	15.3	1	13	35	240	450	2.0	20	14.3	0.42	7.6	28.5	62.5	0.78	0.83	4.17	2.57	21.7	
6	CO.011	15.3	2	61	83	220	450	2.0	20	5.1	0.20	0.0	14.4	82.9	0.87	0.82	--	--	--	
6	CO.011	15.3	3	88	107	240	450	2.0	20	13.5	0.41	5.4	28.3	64.5	0.79	--	4.00	2.83	--	
6	CO.011	15.3	4	133	155	240	450	1.0	20	6.3	0.33	0.4	24.6	71.9	0.82	0.88	--	--	--	
6	CO.011	15.3	5	181	203	240	600	1.0	20	6.7	0.35	0.2	20.5	76.4	0.84	0.89	12.00	3.67	27.3	G.C. Calib
6	CO.011	15.3	6	217	226	240	450	2.0	20	12.0	0.36	5.9	28.6	63.4	0.78	--	4.40	2.43	--	

Table I
(Continued)

SUMMARY OF M3 SBCR RUN RESULTS

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

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

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 C6+ (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	Synfld cc/hr	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf			Olefins C6-C18,X	Comments
												XC4	XC2-C5	XC6+			C3	C4			
7	CO.012	15.8	1	14	36	240	450	2.0	20	13.9	0.43	6.1	25.3	66.9	0.80	0.89	4.00	2.57	17.5		
7	CO.012	15.8	2	62	84	220	450	2.0	20	5.1	0.20	0.0	9.9	88.1	0.89	0.90	--	2.50	--		
7	CO.012	15.8	3	88	92	240	450	2.0	20	13.1	0.41	6.1	24.3	67.9	0.80	--	5.00	2.25	--	Power Fail	
7	CO.012	15.8	4	134	156	240	450	1.0	20	3.9	0.13	4.8	42.4	46.2	0.70	0.85	16.00	3.50	--		
7	CO.012	15.8	5	182	204	240	600	1.0	20	4.3	0.17	0.1	37.7	55.9	0.75	0.82	8.50	3.50	30.8		
7	CO.012	15.8	6	218	227	240	450	2.0	20	7.2	0.15	7.3	43.6	44.7	0.70	--	5.00	3.17	--		
8	CO.015	15.0	1	14	35	240	450	2.0	20	28.3	0.79	12.7	28.5	57.6	0.76	0.80	1.61	1.07	19.6	G.C.Calib	
8	CO.015	15.0	2	61	83	220	450	2.0	20	11.5	0.39	4.4	25.7	69.2	0.81	0.89	3.60	2.14	--		
8	CO.015	15.0	3	97	106	240	450	2.0	20	26.4	0.72	13.2	29.5	56.1	0.75	--	1.69	1.20	--		
8	CO.015	15.0	4	133	155	240	450	1.0	20	11.5	0.57	4.8	25.9	67.8	0.80	0.85	5.60	3.29	--		
8	CO.015	15.0	5	181	191	240	600	1.0	20	12.4	0.69	4.9	17.5	76.9	0.84	0.85	5.20	3.14	30.8	Power Fail	
9	CO.011	15.0	1	13	35	240	450	2.0	20	18.5	0.56	8.8	27.6	62.9	0.78	0.83	3.18	1.85	20.3	G.C.Calib	
9	CO.011	15.0	2	61	82	220	450	2.0	20	6.3	0.26	0.0	14.6	84.9	0.88	0.93	12.00	1.80	--		
9	CO.011	15.0	3	97	107	240	450	2.0	20	16.6	0.49	8.4	29.1	61.7	0.77	--	3.30	2.00	--		
9	CO.011	15.0	4	133	155	240	450	1.0	20	8.0	0.42	1.3	25.6	72.0	0.82	0.87	7.00	2.83	--		
9	CO.011	15.0	5	181	203	240	600	1.0	20	8.7	0.47	1.4	22.9	74.6	0.83	0.87	5.00	2.67	30.5		
9	CO.011	15.0	6	228	229	240	450	2.0	20	14.7	0.44	7.9	28.9	62.4	0.78	--	3.78	1.67	--	Power Fail	
11	CO.017	15.0	1	9	31	240	450	2.0	20	27.2	0.80	11.2	26.5	61.2	0.77	0.80	2.09	1.20	30.8		
11	CO.017	15.0	2	55	79	220	450	2.0	20	11.4	0.46	5.0	10.4	80.4	0.88	0.90	5.00	3.20	--		
11	CO.017	15.0	3	81	103	240	450	2.0	20	25.9	0.76	11.7	26.3	60.9	0.77	--	1.95	1.26	--		
11	CO.017	15.0	4	129	151	240	450	1.0	20	11.6	0.62	5.0	21.1	72.8	0.82	0.86	25.0	2.88	--		
11	CO.017	15.0	5	177	199	240	600	1.0	20	11.6	0.69	4.2	13.9	80.8	0.86	0.86	24.0	1.63	21.0	G.C.Calib	
11	CO.017	15.0	6	213	221	240	450	2.0	20	24.3	0.74	12.1	25.3	62.5	0.78	--	2.47	1.64	--		
12	CO.018	15.6	1	13	35	240	450	2.0	20	33.8	0.87	9.7	33.2	55.4	0.75	0.85	1.81	1.13	21.0	G.C.Calib	
12	CO.018	15.6	2	61	80	220	450	2.0	20	12.6	0.52	2.8	7.8	89.3	0.90	0.88	--	--	--		
12	CO.018	15.6	3	97	107	240	450	2.0	20	27.9	0.72	9.4	34.3	55.3	0.75	--	2.65	2.17	--		
12	CO.018	15.6	4	133	155	240	450	1.0	20	12.4	0.58	3.3	28.3	66.7	0.80	0.86	--	--	--		
12	CO.018	15.6	5	181	203	240	600	1.0	20	13.0	0.62	3.2	26.8	68.2	0.80	0.85	--	--	38.5		
12	CO.018	15.6	6	217	226	240	450	2.0	20	26.4	0.64	10.1	36.5	51.7	0.73	--	2.89	2.05	--		

Table II

SLURRY BUBBLE COLUMN REACTION DATA

EFFECT OF PARTICLE SIZE

	100x400 mesh size	170x400 mesh size
CO Conversion (%)	14.3	18.5
C6+ Rate (kg/kg cat. hr)	0.42	0.56
CH ₄ (wt%)	7.6	8.8
C6+ (wt%)	62.5	62.9
alpha	0.78	0.78

Catalyst: C0.011, 20% Co/SiO₂; weight: ca. 15g

Temperature (°C) = 240

Pressure (psi) = 450

H₂/CO ratio = 2

Total flow rate: ca. 15 L/min, or 3 cm/sec linear velocity

Diluent: N₂: ca. 60%

Table III

DATE: 09/24/93

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
-----	-----	-----	-----
1	240 C	450psi	2.0

- a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.
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 C6+ (kg/kg cat.,hr).
e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-C18,%
---	---	---	---	---	%CH4	%C2-C5	%C6+	---	---	C3	C4	---
5	CO.003	15.1	31.7	0.73	16.7	34.2	47.9	0.71	0.94	1.30	0.60	18.2
6	CO.011	15.3	14.3	0.42	7.6	28.5	62.5	0.78	0.83	4.17	2.57	21.7
7	CO.012	15.8	13.9	0.43	6.1	25.3	66.9	0.80	0.89	4.00	2.57	17.5
8	CO.015	15.0	28.3	0.79	12.7	28.5	57.6	0.76	0.80	1.61	1.07	19.6
9	CO.011	15.0	18.5	0.56	8.8	27.6	62.9	0.78	0.83	3.18	1.85	20.3
11	CO.017	15.0	27.2	0.80	11.2	26.5	61.2	0.77	0.80	2.09	1.20	30.8
12	CO.018	15.6	33.8	0.87	9.7	33.2	55.4	0.75	0.85	1.81	1.13	21.0

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalyst For Runs 11 and 12 screened thru 150 x 400 mesh.

Table IV

SLURRY BUBBLE COLUMN REACTION DATA

ACTIVITY AND SELECTIVITY OF VARIOUS CATALYSTS
AT STANDARD REACTION CONDITIONS

Catalyst	Composition			CO Conv. (%)	C6+ Rate (kg/kg cat. hr)	CH ₄ (wt%)	C6+ (wt%)	Alpha
	Co wt%	Promoter wt%	Support					
Co.003	20%	0.5%Ru, 1%La ₂ O ₃ (n-aqueous, 1 step)	Al ₂ O ₃	31.7	0.73	16.7	47.9	0.94
Co.011	20%	-	SiO ₂	14.3	0.42	7.6	62.5	0.83
Co.012	20%	-	SiO ₂	13.9	0.43	6.1	66.9	0.89
Co.015	20%	0.5%Ru, 1%La ₂ O ₃ (aqueous, 2 steps)	Al ₂ O ₃	28.3	0.79	12.7	57.6	0.80
Co.017	20%	0.5%Ru, 1%La ₂ O ₃ (aqueous, 1 step)	Al ₂ O ₃	27.2	0.80	11.2	61.2	0.80
Co.018	20%	0.5% Ru	Al ₂ O ₃	33.8	0.87	9.7	55.4	0.85

Catalyst weight: ca. 15g

Temperature (°C) = 240

Pressure (psi) = 450

H₂/CO ratio = 2

Total flow rate: ca. 15 L/min, or 3 cm/sec linear velocity

Diluent: N₂: ca. 60%

Table V

DATE: 09/24/93

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H2/CO Ratio
-----	-----	-----	-----
2	220 C	450psi	2.0

a) Total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.

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 C6+ (kg/kg cat., hr).

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

Run No	Cat. No	Cat. wt, g	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-C18, %
					%CH4	%C2-C5	%C6+			C3	C4	
5	CO.003	15.1	13.2	0.45	5.1	23.1	71.3	0.82	0.90	4.55	1.89	--
6	CO.011	15.3	5.1	0.20	0.0	14.4	82.9	0.87	0.82	--	--	--
7	CO.012	15.8	5.1	0.20	0.0	9.9	88.1	0.89	0.90	--	2.50	--
8	CO.015	15.0	11.5	0.39	4.4	25.7	69.2	0.81	0.89	3.60	2.14	--
9	CO.011	15.0	6.3	0.26	0.0	14.6	84.9	0.88	0.93	12.00	1.80	--
11	CO.017	15.0	11.4	0.46	5.0	10.4	80.4	0.88	0.90	5.00	3.20	--
12	CO.018	15.6	12.6	0.52	2.8	7.8	89.3	0.90	0.88	--	--	--

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalyst for Runs 11 and 12 screened thru 150 x 400 mesh.

Table VI

DATE: 09/24/93

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
4	240 C	450psi	1.0

- a) Total flow is ca. 15 L/min. STP, or 3 cm/sec linear gas flow.
 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 C₆+ (kg/kg cat., hr).
 e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt, g	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C ₆ -C ₁₈ , %
					%CH ₄	%C ₂ -C ₅	%C ₆ +			C ₃	C ₄	
5	CO.003	15.1	13.1	0.70	4.2	20.7	73.9	0.83	0.88	6.67	3.70	--
6	CO.011	15.3	6.3	0.33	0.4	24.6	71.9	0.82	0.88	--	--	--
7	CO.012	15.8	3.9	0.13	4.8	42.4	46.2	0.70	0.85	16.00	3.50	--
8	CO.015	15.0	11.5	0.57	4.8	25.9	67.8	0.80	0.85	5.60	3.29	--
9	CO.011	15.0	8.0	0.42	1.3	25.6	72.0	0.82	0.87	7.00	2.83	--
11	CO.017	15.0	11.6	0.62	5.0	21.1	72.8	0.82	0.86	25.00	2.88	--
12	CO.018	15.6	12.4	0.58	3.3	28.3	66.7	0.80	0.86	--	--	--

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalyst for Runs 11 and 12 screened thru 150 x 400 mesh.

Table VII

DATE: 09/24/93

M3 SBCR RUN RESULTS

COMPARISON OF CATALYST ACTIVITY AT SIMILAR RUN CONDITIONS

Period No.	Temp.	Pres.	H ₂ /CO Ratio
-----	-----	-----	-----
5	240 C	600psi	1.0

- a) Total flow is ca.15 L/min. STP, or 3 cm/sec linear gas flow.
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 C₆+ (kg/kg cat.,hr).
e) Alpha: Based on GC analysis of offgas and liquid product.

Run No	Cat. No	Cat. wt,g	Conv. %	Prod. Rate	Selectivity			Alpha GC	Alpha Liq	Olefin/Paraf		Olefins C6-C18, %
					%CH ₄	%C ₂ -C ₅	%C ₆ +			C3	C4	
5	CO.003	15.1	13.4	0.68	3.9	25.3	69.5	0.81	--	5.26	3.45	30.1
6	CO.011	15.3	6.7	0.35	0.2	20.5	76.4	0.84	0.89	12.00	3.67	27.3
7	CO.012	15.8	4.3	0.17	0.1	37.7	55.9	0.75	0.82	8.50	3.50	--
8	CO.015	15.0	12.4	0.69	4.9	17.5	76.9	0.84	0.85	5.20	3.14	30.8
9	CO.011	15.0	8.7	0.47	1.4	22.9	74.6	0.83	0.87	5.00	2.67	30.5
11	CO.017	15.0	11.6	0.69	4.2	13.9	80.8	0.86	0.86	24.00	1.63	21.0
12	CO.018	15.6	13.0	0.62	3.2	26.8	68.2	0.80	0.85	--	--	38.5

Note: Catalyst Run 9 screened thru 170 x 400 mesh.

Catalyst Run 11 screened thru 150 x 400 mesh.

Table VIII

M-3 SBCR CATALYST EXTRACTIONS

<u>Catalyst No.</u> <u>(Support)</u>	<u>Run No.</u>	<u>Charge</u> <u>(H₂ Reduced)</u> <u>wt, gm</u>	<u>Recovered</u> <u>(Oxidized)</u> <u>wt, gm</u>	<u>Charge</u> <u>Particle</u> <u>Size, mvd,</u> <u>microns</u>	<u>Recovered</u> <u>Particle</u> <u>Size, mvd,</u> <u>microns</u>
Co.001 (Al)	1	14.5	12.63	42.02	41.06
Co.001 (Al)	2	16.5	15.18	42.02	40.09
Co.005 (Al)	3	19.5	18.41	85.66	64.53
Co.002 (Al)	4	20.1	20.4	73.61	71.19
Co.003 (Al)	5	15.1	14.54	76.81	72.57
Co.011 (Si)	6	15.3	16.03	107.09 (1)	94.02
Co.012 (Si)	7	15.8	14.73	105.22 (1)	101.37
Co.015 (Al)	8	15.0	15.52	75.63 (1)	74.68
Co.011 (Si)	9	15.0	15.92	79.88 (2)	72.44
Co.016 (Al)	10	15.5	15.72	64.60 (2)	64.38
Co.017 (Al)	11	15.0	15.09	73.14 (3)	69.95
Co.018 (Al)	12	15.6	16.97	62.89 (3)	68.16

- (1) Screened through 100x400 mesh screens.
 (2) Screened through 170x400 mesh screens.
 (3) Screened through 150x400 mesh screens.

Note: The charge weights are in the hydrogen-reduced state and the recovered weights are in the oxidized state. The particle size is reported as the mean volume diameter (mvd) as measured by a Microtrac particle size analyzer.

Figure 1

PARTICLE SIZE DISTRIBUTION OF
CHARGED AND RECOVERED CATALYST NO. Co.012

RCO.012 RUN 7
CATALYST EXTRACT

1222

CATALYST

1212

CO.012 6/30/93

1212

PARTICLE SIZE DISTRIBUTION OF
CHARGED AND RECOVERED CATALYST NO. Co.015

RCO.015-RUN 8 RECOVERED CATALYST	1226	CO.015 calcined 300c	1215
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D-13

PARTICLE SIZE DISTRIBUTION OF
CHARGED AND RECOVERED CATALYST NO. Co.011

RCO 011
RUN 9

1231 RN-23-18A
170x400 mesh

1220

D-14

PARTICLE SIZE DISTRIBUTION OF
CHARGED AND RECOVERED CATALYST NO. Co.017

CO. 017
5006-0220

1248 | CO.017
| 150 X 400

1236 |
|

Esc-exit F2-clr key

Figure 5

PARTICLE SIZE DISTRIBUTION OF
CHARGED AND RECOVERED CATALYST NO. Co.018

CO. 018
RUN 12

1255 | CO.018
|——| 150 X 400 MESH

1254

D-16

END

DATE

FILMED

4/14/94