



DE87006115

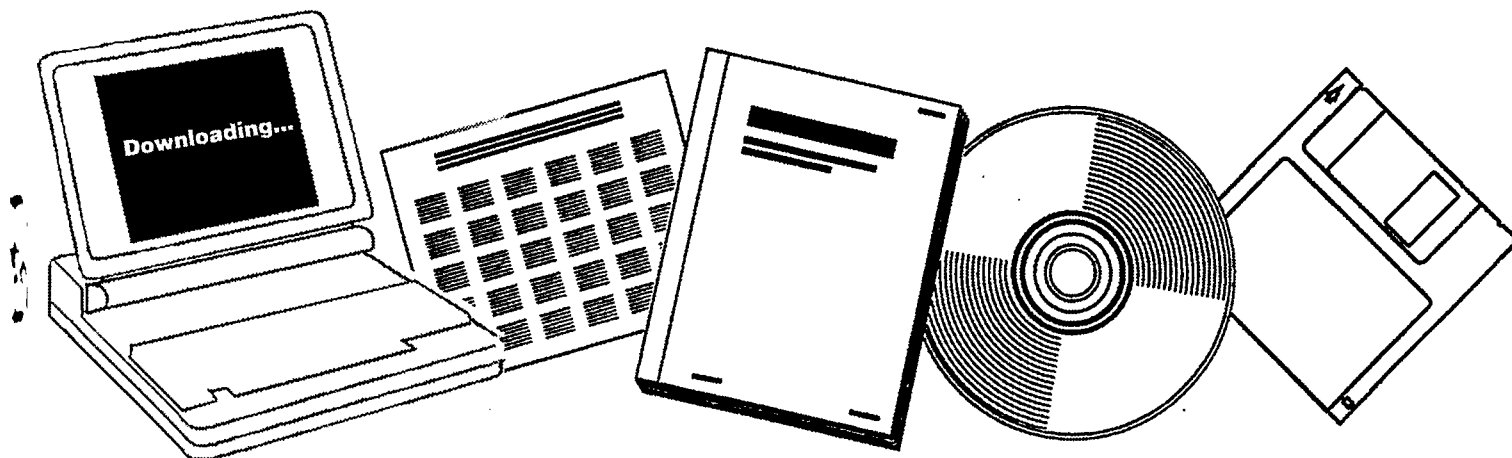
NTIS

One Source. One Search. One Solution.

**NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND
PROCESS CONCEPTS FOR SELECTIVE
TRANSPORTATION FUEL PRODUCTION: QUARTERLY
TECHNICAL PROGRESS REPORT FOR THE PERIOD 1
APRIL-30 JUNE 1986**

**AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA**

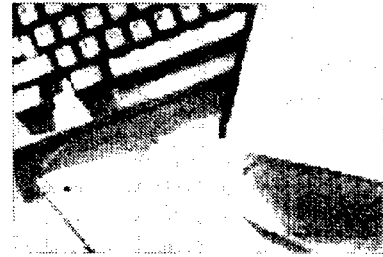
FEB 1987



U.S. Department of Commerce
National Technical Information Service

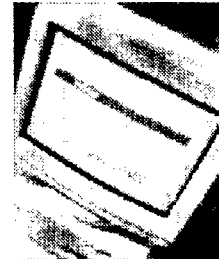
One Source. One Search. One Solution.

NTIS



Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on www.ntis.gov. You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov



U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

DE87006115



DOE/PC/70030--T7

DE87 006115

AIR
PRODUCTS 

NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS

FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD 1 APRIL - 30 JUNE 1986

W. EAMON CARROLL
KENNETH F. ELIEZER
JOHN W. MITCHELL
HOWARD P. WITHERS, JR.

AIR PRODUCTS AND CHEMICALS, INC.

ALLENTOWN, PA 18105

PREPARED FOR UNITED STATES DEPARTMENT OF ENERGY

UNDER CONTRACT NO. DE-AC22-84PC70030

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 

DISCLAIMER

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

PATENT HOLD

This documented copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for the use in performance of work under contracts with the United States Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request from the Chief, Office of Patent Counsel, United States Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

EXECUTIVE SUMMARY

In the seventh, and final, quarter of the Air Products and Chemicals, Inc./United States Department of Energy Contract, "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production", work continued on the three major tasks: Task 2 -- Development of Improved Supported Catalyst Compositions, Task 3 -- Slurry Reactor Kinetic Studies, and Task 4 -- Fuel Product Characterization.

To examine the importance of surface area effects on the activity enhancement of the Co/Zr/silica catalyst, a Co/Zr/silica catalyst having the same surface area as the Co/Zr/alumina catalyst was tested in the fixed bed reactor. The bulk and specific activities of the silica catalyst were 50-60% greater than those of the alumina catalyst at similar conditions. The high surface silica catalyst, however, was still the most active with 30-50% greater bulk activity than the low surface silica catalyst. Thus silica does provide an inherently more active catalyst than alumina but some of the enhancement that was initially observed was due to the increased surface area. The hydrocarbon selectivity was similar for both high and low surface area Co/Zr/silica catalysts

The effect of increasing metal loadings on the performance of the Co/Zr/silica catalyst was examined with tests of 11.0% and 14.4% Co catalysts in the fixed bed reactor. Comparing bulk activity trends as the metal loading was increased reveals that relatively small changes occurred on going from 3.5 to 11.0% Co at 220°C and 240°C, while upon increasing the Co loading to 14.4%, a large decline in bulk activity occurred at all temperatures. The 11.0% Co catalyst gave the highest syngas conversion (52%) at 220°C of any catalyst tested at this temperature during this contract. Selectivity to liquid fuel product (C₅₋₂₃) declined with increasing Co loading with an overall flattening of the hydrocarbon distribution.

Slurry screening tests were performed on two catalysts. One was a cobalt on silica catalyst without any added promoter atoms such as Zr or Ti. The slurry phase tests showed that this catalyst had lower specific activity than the catalysts with Zr/Co ratios of 1.9 and 0.5. This confirmed the gas phase tests which showed lower activities with less Zr. The other screening test was a Zr promoted cobalt on silica catalyst with a high loading of Co. As was true in the gas phase tests with this catalyst, the slurry phase tests showed lower specific activity with the high load catalyst (16.4 wt.% Co) compared to the basecase catalyst (4.9 wt.% Co).

The extended slurry test which was begun in December 1985 was completed in June. During this quarter, a series of experiments was run to try to determine reaction kinetics. The last experiment was an attempt to regenerate the catalyst using pure H₂. In fact, no change was made in activity. Including both the stability and kinetic tests, the reactor was operated for 4417 hours with the same catalyst charge. Interestingly, when the reactor was shut down it was discovered that the "slurry" was a powdery substance resembling catalyst only and no liquid phase. Due to the low wax yields at the end of the run during the 280°C tests, the wax may have had a net loss through misting, evaporation and/or hydrocracking.

The data from the extended slurry tests were fit to five different kinetic rate equations. The equation which fit the best was one which contained a water inhibition term. This is reasonable considering the high water concentrations resulting from the low shift activity of the Co catalyst used. Another result of the data was the calculation of an activation energy of 29,200 cal./g.mol. based upon the experiments performed at different temperatures during the run.

The spent catalyst from the extended slurry test of the Co/Zr/SiO₂ catalyst (Test 8862-1-31) was found to contain 43.2% carbon and 2.4% hydrogen. This indicated a significant amount of coke formation, which probably occurred after the loss of slurry medium when the reactor skin temperature became excessive. This coke contributed to poor catalyst performance and could not be removed by a hydrogen treatment.

A second sample of liquid organic product was collected from the extended slurry test for testing as a diesel fuel. This second sample, collected at different conditions from the first sample, showed little difference in properties. The second sample also met all the requirements for the highest quality diesel fuel except for viscosity and cloud point, for which there were only small deviations from the specifications.

TABLE OF CONTENTS

	<u>PAGE</u>
1.0 <u>INTRODUCTION</u>	1
2.0 <u>OBJECTIVE</u>	3
3.0 <u>RESULTS AND DISCUSSION</u>	5
3.1 Task 1 -- Project Work Plan	5
3.2 Task 2 -- Development of Improved Supported Catalyst Compositions	5
(a) Catalyst Preparation	5
(b) Gas Phase Screening	5
(c) Slurry Reactor Tests	8
(d) Catalyst Characterization	15
3.3 Task 3 -- Slurry Reactor Kinetic Studies	15
3.4 Task 4 -- Fuel Product Characterization	17
4.0 <u>EXPERIMENTAL</u>	17
4.1 Task 2 -- Development of Improved Supported Catalyst Compositions	17
(a) Catalyst Preparation	17
(b) Gas Phase Screening	18
(c) Slurry Reactor Tests	18
(d) Catalyst Characterization	19
5.0 <u>REFERENCES</u>	20
6.0 <u>ACKNOWLEDGEMENTS</u>	21

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	Gas Phase Tests Summary	22
2	Effect of Surface Area - Gas Phase Tests	24
3	Effect of Metal Loading - 11.0% Co	25
4	Effect of Metal Loading - 14.4% Co	26
5	Analysis of Slurry - Phase Fischer - Tropsch Synthetic Diesel Fuel	27
6	Comparative Catalyst Test Data - Slurry Tests	28
<u>Slurry Screening Summary and Mass Balance Results for</u>		
<u>Co₂(CO)₈/SiO₂ -- 8862-80-49</u>		
7	Slurry Screening Summary	32
8	Mass Balance Process Conditions and Product Summary -- Sample 3	33
9	Hydrocarbon Product Distribution -- Sample 3	34
10	Mass Balance Process Conditions and Product Summary -- Sample 6	36
11	Hydrocarbon Product Distribution -- Sample 6	37
12	Mass Balance Process Conditions and Product Summary -- Sample 9	39
13	Hydrocarbon Product Distribution -- Sample 9	40
14	Mass Balance Process Conditions and Product Summary -- Sample 12	42
15	Hydrocarbon Product Distribution -- Sample 12	43
16	Mass Balance Process Conditions and Product Summary -- Sample 15	45
17	Hydrocarbon Product Distribution -- Sample 15	46
18	Mass Balance Process Conditions and Product Summary -- Sample 18	48
19	Hydrocarbon Product Distribution -- Sample 18	49
20	Mass Balance Process Conditions and Product Summary -- Sample 21	51
21	Hydrocarbon Product Distribution -- Sample 21	52
22	Mass Balance Process Conditions and Product Summary -- Sample 23	54
23	Hydrocarbon Product Distribution -- Sample 23	55
24	Mass Balance Process Conditions and Product Summary -- Sample 27	57
25	Hydrocarbon Product Distribution -- Sample 27	58
26	Mass Balance Process Conditions and Product Summary -- Sample 30	60
27	Hydrocarbon Product Distribution -- Sample 30	61
<u>Slurry Screening Summary and Mass Balance Results for</u>		
<u>Co₂(CO)₈/Zr(OPr)₄/SiO₂ -- 9093-10-58</u>		
28	Slurry Screening Summary	63
29	Mass Balance Process Conditions and Product Summary -- Sample 2	64
30	Hydrocarbon Product Distribution -- Sample 2	65

LIST OF TABLES (Continued)

<u>TABLE</u>		<u>PAGE</u>
31	Mass Balance Process Conditions and Product Summary -- Sample 4	67
32	Hydrocarbon Product Distribution -- Sample 4	68
33	Mass Balance Process Conditions and Product Summary -- Sample 7	70
34	Hydrocarbon Product Distribution -- Sample 7	71
35	Mass Balance Process Conditions and Product Summary -- Sample 10	73
36	Hydrocarbon Product Distribution -- Sample 10	74
37	Mass Balance Process Conditions and Product Summary -- Sample 12	76
38	Hydrocarbon Product Distribution -- Sample 12	77
 <u>Extended Slurry Test Summary and Mass Balance Results for $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ -- 8862-1-31</u>		
39	Extended Slurry Test Summary	79
40	Mass Balance Process Conditions and Product Summary -- Sample 94	83
41	Hydrocarbon Product Distribution -- Sample 94	84
42	Mass Balance Process Conditions and Product Summary -- Sample 98	86
43	Hydrocarbon Product Distribution -- Sample 98	87
44	Mass Balance Process Conditions and Product Summary -- Sample 100	89
45	Hydrocarbon Product Distribution -- Sample 100	90
46	Mass Balance Process Conditions and Product Summary -- Sample 104	92
47	Hydrocarbon Product Distribution -- Sample 104	93
48	Mass Balance Process Conditions and Product Summary -- Sample 107	95
49	Hydrocarbon Product Distribution -- Sample 107	96
50	Mass Balance Process Conditions and Product Summary -- Sample 109	98
51	Hydrocarbon Product Distribution -- Sample 109	99
52	Mass Balance Process Conditions and Product Summary -- Sample 112	101
53	Hydrocarbon Product Distribution -- Sample 112	102
54	Mass Balance Process Conditions and Product Summary -- Sample 115	104
55	Hydrocarbon Product Distribution -- Sample 115	105
56	Mass Balance Process Conditions and Product Summary -- Sample 118	107
57	Hydrocarbon Product Distribution -- Sample 118	108
58	Mass Balance Process Conditions and Product Summary -- Sample 121	110
59	Hydrocarbon Product Distribution -- Sample 121	111
60	Mass Balance Process Conditions and Product Summary -- Sample 124	113
61	Hydrocarbon Product Distribution -- Sample 124	114
62	Mass Balance Process Conditions and Product Summary -- Sample 128	116
63	Hydrocarbon Product Distribution -- Sample 128	117

LIST OF TABLES (Continued)

<u>TABLE</u>		<u>PAGE</u>
64	Mass Balance Process Conditions and Product Summary -- Sample 131	119
65	Hydrocarbon Product Distribution -- Sample 131	120
66	Mass Balance Process Conditions and Product Summary -- Sample 134	122
67	Hydrocarbon Product Distribution -- Sample 134	123
68	Mass Balance Process Conditions and Product Summary -- Sample 136	125
69	Hydrocarbon Product Distribution -- Sample 136	126
70	Mass Balance Process Conditions and Product Summary -- Sample 140	128
71	Hydrocarbon Product Distribution -- Sample 140	129
72	Mass Balance Process Conditions and Product Summary -- Sample 142	131
73	Hydrocarbon Product Distribution -- Sample 142	132
74	Mass Balance Process Conditions and Product Summary -- Sample 148	134
75	Hydrocarbon Product Distribution -- Sample 148	135
76	Mass Balance Process Conditions and Product Summary -- Sample 151	137
77	Hydrocarbon Product Distribution -- Sample 151	138
78	Mass Balance Process Conditions and Product Summary -- Sample 153	140
79	Hydrocarbon Product Distribution -- Sample 153	141
80	Mass Balance Process Conditions and Product Summary -- Sample 155	143
81	Hydrocarbon Product Distribution -- Sample 155	144
82	Mass Balance Process Conditions and Product Summary -- Sample 158	146
83	Hydrocarbon Product Distribution -- Sample 158	147
84	Mass Balance Process Conditions and Product Summary -- Sample 162	149
85	Hydrocarbon Product Distribution -- Sample 162	150
86	Mass Balance Process Conditions and Product Summary -- Sample 164	152
87	Hydrocarbon Product Distribution -- Sample 164	153
88	Mass Balance Process Conditions and Product Summary -- Sample 167	155
89	Hydrocarbon Product Distribution -- Sample 167	156
90	Mass Balance Process Conditions and Product Summary -- Sample 171	158
91	Hydrocarbon Product Distribution -- Sample 171	159
92	Mass Balance Process Conditions and Product Summary -- Sample 173	161
93	Hydrocarbon Product Distribution -- Sample 173	162
94	Mass Balance Process Conditions and Product Summary -- Sample 176	164
95	Hydrocarbon Product Distribution -- Sample 176	165
96	Support Properties	167
97	Selected Kinetic Functionalities	168
98	Summary of Fitted Kinetic Parameters	169

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	Effect of Surface Area on Bulk Activity and Selectivity	170
2	Effect of Cobalt Loading on Bulk Activity of Co/Zr/SiO ₂ Catalyst	171
<u>Co₂(CO)₈/SiO₂ Slurry Test Results -- 8862-80-49</u>		
3	Hydrocarbon Weight Distribution -- Sample 3	172
4	Hydrocarbon Weight Distribution -- Sample 6	173
5	Hydrocarbon Weight Distribution -- Sample 9	174
6	Hydrocarbon Weight Distribution -- Sample 12	175
7	Hydrocarbon Weight Distribution -- Sample 15	176
8	Hydrocarbon Weight Distribution -- Sample 18	177
9	Hydrocarbon Weight Distribution -- Sample 21	178
10	Hydrocarbon Weight Distribution -- Sample 23	179
11	Hydrocarbon Weight Distribution -- Sample 27	180
12	Hydrocarbon Weight Distribution -- Sample 30	181
<u>Co₂(CO)₈/Zr(OPr)₄/SiO₂ Slurry Test Results -- 9093-10-58</u>		
13	Hydrocarbon Weight Distribution -- Sample 2	182
14	Hydrocarbon Weight Distribution -- Sample 4	183
15	Hydrocarbon Weight Distribution -- Sample 7	184
16	Hydrocarbon Weight Distribution -- Sample 10	185
17	Hydrocarbon Weight Distribution -- Sample 12	186
<u>Co₂(CO)₈/Zr(OPr)₄/SiO₂ Extended Slurry Test Results -- 8862-1-31</u>		
18	Hydrocarbon Weight Distribution -- Sample 94	187
19	Hydrocarbon Weight Distribution -- Sample 98	188
20	Hydrocarbon Weight Distribution -- Sample 100	189
21	Hydrocarbon Weight Distribution -- Sample 104	190
22	Hydrocarbon Weight Distribution -- Sample 107	191
23	Hydrocarbon Weight Distribution -- Sample 109	192
24	Hydrocarbon Weight Distribution -- Sample 112	193
25	Hydrocarbon Weight Distribution -- Sample 115	194
26	Hydrocarbon Weight Distribution -- Sample 118	195
27	Hydrocarbon Weight Distribution -- Sample 121	196
28	Hydrocarbon Weight Distribution -- Sample 124	197
29	Hydrocarbon Weight Distribution -- Sample 128	198
30	Hydrocarbon Weight Distribution -- Sample 131	199
31	Hydrocarbon Weight Distribution -- Sample 134	200
32	Hydrocarbon Weight Distribution -- Sample 136	201
33	Hydrocarbon Weight Distribution -- Sample 140	202
34	Hydrocarbon Weight Distribution -- Sample 142	203
35	Hydrocarbon Weight Distribution -- Sample 148	204
36	Hydrocarbon Weight Distribution -- Sample 151	205
37	Hydrocarbon Weight Distribution -- Sample 153	206
38	Hydrocarbon Weight Distribution -- Sample 155	207

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>PAGE</u>
39	Hydrocarbon Weight Distribution -- Sample 158	208
40	Hydrocarbon Weight Distribution -- Sample 162	209
41	Hydrocarbon Weight Distribution -- Sample 164	210
42	Hydrocarbon Weight Distribution -- Sample 167	211
43	Hydrocarbon Weight Distribution -- Sample 171	212
44	Hydrocarbon Weight Distribution -- Sample 173	213
45	Hydrocarbon Weight Distribution -- Sample 176	214
46	Bulk Activity Maintenance for Extended Test	215
47	Linear Fit for Kinetic Model 1, 260°C	216
48	Linear Fit for Kinetic Model 2, 260°C	217
49	Linear Fit for Kinetic Model 4, 260°C	218
50	Parity Plot for Kinetic Model 1, 260°C	219
51	Parity Plot for Kinetic Model 2, 260°C	220
52	Parity Plot for Kinetic Model 4, 260°C	221
53	Parity Plot for Kinetic Model 5, 260°C	222
54	Linear Fit for Kinetic Model 4, 280°C	223
55	Parity Plot for Kinetic Model 4, 280°C	224
56	Arrhenius Plot - Extended Slurry Test -- 8862-1-31	225
57	Catalyst Deactivation - Extended Slurry Test -- 8862-1-31	226
APPENDIX	Energy Input from Impeller versus Gas Expansion	227

1.0 INTRODUCTION

The future use of coal as a transportation fuel will depend on the development of an economical and energy efficient liquefaction process. The two most advanced processes are the direct liquefaction route involving the dissolution of coal in a solvent aided by a mild hydrogenation and the indirect route in which coal is first gasified to synthesis gas followed by the Fischer-Tropsch reaction. The indirect liquefaction process is the only one currently practiced commercially and, in this respect, has a firm data base of practical experience.

The Fischer-Tropsch reaction, in which carbon monoxide is reduced by hydrogen and polymerized, produces hydrocarbons with a broad range of molecular weights, from methane to paraffin waxes. This creates the need for further downstream processing such as hydrocracking and light olefin oligomerization to maximize the yield of liquid fuel product. Since the discovery of the Fischer-Tropsch reaction, extensive research has been aimed at controlling the product selectivity in order to minimize downstream refining and still remains a prime target for innovation. Previous research has shown that selectivity is mainly controlled by catalyst composition and process conditions. Despite the vast effort in catalyst research, no catalyst has been developed that yields a narrow product distribution of only gasoline or diesel fuel. Because of this, product selectivity has been more successfully controlled by manipulating process conditions.

Since the Fischer-Tropsch reaction is exothermic, control of the reaction heat plays a major role in determining product selectivity. Suspending the catalyst in a liquid medium offers the best means of heat transfer and temperature control. Thus slurry phase operation has been shown to give improved liquid product selectivity mainly by lowering the light gas yield. The amount of data from slurry phase operation, however, is limited to only a few studies and significant differences have been reported in yields, catalyst life and ease of operation. One consistent observation is the lower gas yields and improved gasoline and diesel product selectivity. The improved temperature control has allowed this technology to be useful in converting carbon monoxide-rich synthesis gas from the latest coal gasifiers.

Slurry phase operation also appears to be more amenable to scale-up. Much research remains to be done to fully determine the potential of slurry phase Fischer-Tropsch processing and its further development is an important part in our country's program to establish viable technology for converting coal to conventional hydrocarbon fuels.

Under prior contract number DE-AC22-80PC30021 with the Department of Energy, Air Products and Chemicals, Inc. developed several new slurry-phase Fischer-Tropsch catalyst systems that provided enhanced selectivity to liquid fuel products. One group of these catalysts included Co or Ru carbonyls on a specially promoted/modified support. To further develop and improve these catalyst systems, Air Products, by the current contract to DOE, has begun a program to reproduce, evaluate and characterize these catalysts in detail. Examination of the catalyst kinetics in the slurry phase along with fuel product characterization will be used to improve process design. Knowledge gained from these studies will provide a basis for the development of novel improved catalysts and process concepts for the selective production of liquid transportation fuels from synthesis gas. Work accomplished in the seventh, and final, quarter is described in this report.

2.0 OBJECTIVE

The major goal of this project is to thoroughly investigate the preparation, characterization and performance of metal carbonyl cluster-based catalysts for use in slurry phase Fischer-Tropsch technology. As this understanding of catalyst behavior increases, improved catalysts will be designed and process concepts developed toward increasing catalyst activity, lifetime and selective production of liquid fuel product. The objectives will be addressed by the following four tasks:

Task 1 -- Develop a project work plan which presents the detailed activities to be performed in achieving the objectives of this project. This task has been completed in the first quarter.

Task 2 -- Develop improved supported cobalt and ruthenium carbonyl cluster-based catalysts by utilizing the promising leads discovered during prior work at Air Products under DOE contract number DE-AC22-80PC30021, which has shown that metal carbonyls supported on modified aluminas exhibit high activity, stability, and good selectivity to liquid fuels in the slurry phase Fischer-Tropsch process. New catalyst compositions designed to give enhanced selectivity to liquid fuels will also be developed.

In this task, catalysts will be evaluated and tested for their potential to convert synthesis gas into liquid hydrocarbon fuels. Catalysts will be studied by a combination of tests in stirred and fixed-bed reactors and will be evaluated on the basis of activity, selectivity, stability and aging. In addition, catalysts will be characterized by surface and bulk analyses.

Improvements in these catalysts will focus predominantly upon:

- o Increasing catalyst activity
- o Improving product selectivity for liquid fuels and reducing the yield of methane
- o Developing catalyst systems active at high CO:H₂ ratios
- o Incorporating water-gas shift activity, either directly in the catalyst or utilizing a mixture of catalysts in the slurry

Task 3 -- The baseline catalyst compositions derived from both cobalt and ruthenium carbonyl clusters will be used to establish baseline slurry Fischer-Tropsch rate constants and activation energies. Then the more active and selective slurry catalyst compositions, identified under Task 2, will also be used in deriving slurry FT kinetic parameters. An existing backmixed CSTR model will be used in fitting the kinetic parameters. The kinetic parameters obtained will then be input to a three-phase bubble column computer model in order to predict conversions and space time yields in commercial scale bubble column units under a range of operating conditions.

An attempt will be made to determine kinetic expressions that describe the rate of formation of individual products or product fractions. This will be used to predict space time yields of individual product components or fuel fractions in a commercial scale bubble column.

Finally, mechanistic concepts will be examined, such as olefin reincorporation into growing chains, by adding small amounts of olefins to the feed and determining the effect on product selectivities.

Task 4 -- In this task, hydrocarbon product fractions, accumulated from some of the longer slurry tests of the improved catalysts, will be collected under constant process conditions and subjected to a series of tests to evaluate their properties as specification fuel.

3.0 RESULTS AND DISCUSSION

3.1 Task 1 -- Project Work Plan

This task was completed and reported on in the first quarter report.

3.2 Task 2 -- Development of Improved Supported Catalyst Compositions

(a) Catalyst Preparation

(i) Co₂(CO)₈/Zr(OPr)₄/SiO₂ (Catalyst #8466-58)

The effect of increasing the Co and Zr loadings on the performance of the Co/Zr silica catalyst was studied this quarter by first examining this 11.0% Co, 7.47% Zr catalyst. This was a 200% increase in Co loading but only a 12% increase in Zr loading. There were several reasons for not keeping the Co-to-Zr ratio at 0.53, which was the ratio used in the basecase catalyst. One reason was based on the results of examining the effect of Co/Zr ratio on performance, which showed that the best bulk activity was achieved when the Co/Zr ratio was between 1.0 and 2.0. A second reason was that we wanted to prepare a Co/Zr/silica catalyst having a composition analogous to that used by Shell Oil Co. in their Middle Distillate ProcessTM but prepared by our own method. This would enable us to make a direct comparison between the two different preparation methods. The catalyst was prepared using our standard impregnation procedure. The addition of the Co₂(CO)₈ required three impregnations.

(ii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ (Catalyst #8466-63)

A further increase in metal loadings was examined with the preparation of this 14.4% Co, 10.2% Zr catalyst. This was a 30% increase over the 11.0% Co catalyst described above. This composition was somewhat similar to the original German commercial Co/Kieselguhr catalyst in that the Co/support ratio is 0.5. The catalyst was prepared by impregnation to incipient wetness, with the Co₂(CO)₈ addition requiring 4 impregnations.

(b) Gas Phase Screening

All of the catalysts screened in the fixed bed reactor this quarter were activated using a pure H₂ procedure as described in Section 4.1b. Specific run conditions did vary somewhat and are documented accordingly. Gas phase performance data is summarized in Table 1.

(i) Co₂(CO)₈/Zr(OPr)₄/SiO₂-Run #7743-16-55, Catalyst #8465-55

The silica-supported Co₂(CO)₈/Zr(OPr)₄ catalyst was previously shown to yield improved performance compared to alumina-supported catalysts. Since the silica catalyst had a 50% greater surface area than the alumina catalyst, it was necessary to determine if the enhanced activity was a result of inherent differences between the supports, such as metal-support interactions, or simply due to the increase in surface area. The gas phase test of this Co/Zr/SiO₂ catalyst, which had the same surface area as the basecase Co/Zr/Al₂O₃ catalyst, was designed to answer that question. Besides the 3 standard test conditions, 2 other conditions were tested, which were analogous to conditions used by Shell Oil in their Middle Distillate Process™ (1) and used in our test for comparative purposes.

The results of this test are tabulated and compared with those of the basecase Co/Zr/Al₂O₃ catalyst and high surface area Co/Zr/SiO₂ catalyst in Table 2. The results are compared graphically in Figure 1. Both the bulk and specific activities of the low surface area silica catalyst were 50 to 60% greater than those of the alumina catalyst at similar conditions. The high surface silica catalyst, however, was still the most active with 30 to 50% greater bulk activity than the low surface silica catalyst. Thus silica does provide an inherently more active catalyst than alumina but some of the enhancement that was initially observed was due to the higher surface area silica. The improved activity with silica may be due to silica's lower reactivity toward metal carbonyls, thus allowing the metal to remain in the active state (2).

The low surface silica catalyst showed similar trends in hydrocarbon selectivity as the high surface silica catalyst, with the best overall liquid fuels selectivity (C₅-23) obtained at 240°C.

The final two test conditions shown in Table 1 were done at lower CO/H₂ ratios and high space velocities. The result was a shift in hydrocarbon selectivity to methane and light gases with total fuels selectivity < 50%. Only a slight increase in bulk activity from 21 to 24 moles syngas/kg cat/hr was achieved by lowering the CO/H₂ ratio from 1.0 to 0.5 at 220°C.

(ii) Co₂(CO)₈/Zr(OPr)₄/SiO₂-Run #7743-27-58, Catalyst #8466-58

The effect of increasing the metal loadings on the performance of the Co/Zr/SiO₂ catalyst was initiated by testing this 11.0% Co, 7.4% Zr catalyst.

Results from the fixed-bed reactor are shown in Table 3, along with the data from the lower loading Co/Zr/ silica catalyst and the similar loading Co/Zr/alumina catalyst. Increasing the cobalt loading resulted in a 39% boost in bulk activity to 43 moles syngas/kg cat/hr at 220°C. At 240°C, however, there was no increase in bulk activity compared to the lower loading catalyst (#8466-18) at the same temperature. Surprisingly, at 260°C, there was a 14% decline in bulk activity to 64 moles syngas/kg cat/hr compared to catalyst #8466-18 at 260°C. These trends are related to the higher bulk density of the heavily loaded catalyst and to the relatively small change in syngas conversion over the temperature range. A 52% syngas conversion at 220°C was the highest observed for any catalyst to date at this temperature. Specific activities were all lower than those of the 3.5% Co catalyst, which was expected because of lower metal dispersion resulting from increasing the metal loading. When compared to the 10.85% Co/Zr/Al₂O₃ catalyst, this 11.0% Co/Zr/SiO₂ catalyst showed a 45 to 140% increase in bulk activity and 30 to 100% increase in specific activity.

Hydrocarbon selectivity did not compare favorably with either the 3.5% Co/silica catalyst or the 10.8% Co/alumina catalyst as shown in Table 3. Liquid fuel selectivity (C₅₋₂₃) was never greater than 56%, which was obtained at the lowest temperature, and the wax (C₂₄₊) selectivity was high compared to other catalysts. As the temperature was increased to 240°C and 260°C, the methane selectivity became quite large.

Two conditions analogous to those in the Shell patent (1) were examined for direct comparisons. At 220°C, our CO conversion of 56% was low compared to their 85%, however the bulk activity of our catalyst was 79 moles syngas/kg cat/hr, which was not significantly lower than the 91 moles syngas/kg cat/hr for the Shell catalyst.

(iii) Co₂(CO)₈/Zr(OPr)₄/SiO₂-Run #7743-39-63, Catalyst #8862-63

A further increase in the Co and Zr loadings was examined by testing this 14.4% Co/10.2% Zr on silica catalyst.

The gas phase activity of the 14.4% Co catalyst was even less than that of the 11.0% Co catalyst and continued the trend of decreasing activity with increasing metal loading on silica. Data from the three Co/Zr/SiO₂ catalysts having different metal loadings is compared in Table 4. The bulk activities of these three catalysts are compared graphically in Figure 2.

Bulk activity of the 14.4% Co catalyst varied over a narrow range of 21 to 36 moles syngas/kg cat/hr. Specific activity never exceeded 0.10 moles CO/mol Co/min. for this heavily loaded catalyst. Comparing the bulk activity trends as the metal loading was increased reveals that relatively small changes occurred on going from 3.5 to 11.0% Co at 220° and 240°C, while upon increasing the Co loading to 14.4% a large decline in bulk activity occurred at all temperatures. This suggests that with further work perhaps the 11.0% Co catalyst can be optimized to give bulk activities similar to the Shell catalyst.

Bulk catalyst density also increased as the metal loading was increased. Since the catalyst bed volume was 10-cc for each test the actual weight of cobalt in the reactor increased by a larger factor than the weight percent metal loadings did and the space velocity based on the weight of cobalt decreased. Perhaps it may have been more accurate to do the activity comparisons using the same weight hourly space velocity for each test.

Methane selectivity was fairly high at 14-18%, while liquid fuels selectivity (C₅₋₂₃) ranged from 53 to 64%. The best selectivity was obtained at 240°C. Overall the catalyst having the lowest cobalt loading was the best in terms of activity and selectivity.

(c) Slurry Reactor Tests

During this quarter, slurry screening tests were performed on two catalysts. Also, the extended test that was begun in December 1985 was continued. All of the tests were conducted in 1-liter reactors. In the screening tests, the operating parameters were varied to determine the conditions necessary for optimum catalyst performance. The primary objectives of the extended test were to examine performance stability at constant operating conditions and to obtain samples for fuel characterization studies. These objectives were satisfied during the previous quarter, so the focus of the extended test changed to collecting data for the kinetic studies.

The two catalysts used in the screening tests were:

- o A cobalt on silica catalyst without any added promoters such as Zr or Ti which had been tested previously. The gas phase tests showed a lower specific activity with less Zr. This trend was observed in slurry run 8862-41-46 (see section 3.2 from the Jan-Mar 1985 Quarterly Report). The test this quarter was conducted to confirm this trend.

- o A Zr-promoted, cobalt on silica catalyst with a high loading of Co. The catalyst is called "high load" because the Co loading was more than triple the loading of the basecase Co/Zr/silica catalyst. In gas phase tests, the high Co loading resulted in lower specific activities than the lower Co loadings. This test was done to determine whether this trend would be true in the slurry phase test.

Selected results from the slurry tests are listed in Table 6, along with representative results of all previous slurry tests from this contract for comparison.

(i) Co₂(CO)₈/SiO₂--Test #8862-80-49, Catalyst #8466-49

The basecase Zr-promoted, Co on silica catalyst used for slurry run 8670-11-18 had a Zr/Co ratio of 1.9. In the Jan-Mar 1986 quarter, slurry run number 8862-41-46 tested a catalyst with a Zr/Co ratio of 0.5. The cobalt on silica catalyst test described here used a catalyst with no Zr. The gas phase tests and the previous slurry phase tests consistently showed that lower Zr/Co ratios resulted in lower bulk activity. That trend continued with the current slurry test. The selectivity to liquid fuels (C₅ - C₂₃) is clearly higher with the Zr-free catalyst. This differs from the comparison of the two previous Co/Zr catalysts which showed little change in liquid fuels selectivity. The activation procedure is described in Section 4.1 and the activity, conversion and selectivity data of this screening test are summarized in Table 7. The data for each mass balance sample are listed in Tables 8 - 27 and hydrocarbon distributions are illustrated in Figures 3 - 12.

The initial operating temperature (Samples 3-12) for this catalyst was 240°C. The pressure was held constant for all runs at 300 psig. The first four mass balances were taken at the following conditions:

<u>Sample #</u>	<u>CO/H₂ (mol. ratio)</u>	<u>SV (L/g cat/hr.)</u>
3	0.49	2.0
6	0.49	1.0
9	1.0	1.0
12	1.1	2.0

These were the same conditions and the same order that was run for the catalyst with Zr/Co of 0.5. At every point bulk and specific activity were lower for the catalyst without Zr. On average, the specific activity for the current catalyst was 54% of that for the 0.5 Zr/Co catalyst. The test conditions for sample 9 provided the greatest selectivity to liquid fuels (C₅ - C₂₃) for both catalysts: current = 75.0, previous = 68.9 wt%. Selectivity to liquid fuel was higher with the Zr-free catalyst at each point.

The next four runs were conducted at 260°C. Again, these were in the same order as the Zr/Co = 0.5 catalyst.

<u>Sample #</u>	<u>CO/H₂</u> <u>(mol. ratio)</u>	<u>SV</u> <u>(L/g cat/hr.)</u>
15	1.0	2.0
18	1.0	1.0
21	0.49	1.0
23	0.49	2.0

The zirconium promoter consistently boosted the specific activity. The increase averaged 64%. The selectivity to liquid fuels was approximately equal for the two catalysts when CO/H₂ = 1.0, but was much better without Zr promoter when CO/H₂ = 0.5.

The next experiment (sample 27) was a deactivation check run at 240° with the feed conditions the same as sample 6. The bulk activity had decreased by 19% and specific activity by 8%. Selectivity had shifted to the C₂ - C₄ range (29.2% vs. 15.4%) with a significant reduction in liquid fuels (45.3% vs. 68.7%).

Finally, the temperature was raised to 280°C with pressure = 300 psig, CO/H₂ = 1.0 mol. ratio, and SV = 1.0 L/g.cat./hr. This set of conditions was not tested with the Zr/Co = 0.5 catalyst. However, sample 51 of the Zr/Co = 1.9 catalyst (slurry run #8670-11-18) was at these conditions. Specific activity was reduced from 0.188 to 0.093 mol CO/mol Co/min without the promoter.

(ii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ - High Load
Test #9093-10-58, Catalyst #8466-58

This was the last catalyst to be tested under this contract. Due to lack of time, the range of conditions tested was less than was generally done for the slurry screening tests. The reduced catalyst contained 16.4wt% Co and 11.5wt% Zr. This compares to 4.9wt% Co and 9.3wt% Zr for the basecase Co/Zr on silica catalyst used for slurry run #8670-11-18. A comparison of the two catalyst in the slurry phase tests demonstrated agreement with the gas phase result of lower specific activity (mol. CO/mol Co/min.) with higher Co loadings. The activation procedure is described in Section 4.1, and the activity, conversion and selectivity data of this screening test are summarized in Table 28. The data for each mass balance sample are listed in Tables 29 - 38 and hydrocarbon distributions are illustrated in Figures 13 - 17.

The space velocity was maintained at 2.0 L/g. cat./hr throughout the test, as was pressure at 300 psig. Two runs were conducted at 240°C, two at 260°C and a deactivation check run at the end at 240°C. The CO/H₂ feed ratio was varied between 0.49 and 1.0. At every comparable point with slurry run #8670-11-18, the high load catalyst showed lower specific activity, bulk activity and conversion (% CO + H₂). For example, sample 7 of the high load test was operated at the same conditions as sample 39 of slurry test #8670-11-18. The specific activities were 0.068 and 0.299 mol CO/mol Co/min, respectively. Similarly, bulk activity was 32.2 vs 44.8 mol. syngas/kg. cat./hr.

Slurry run #8670-11-18 had a Zr/Co ratio of 1.9 compared to 0.7 for the current catalyst. It has been shown that a reduction in the Zr/Co ratio reduces catalyst activity. To insure that this is not the cause for the reduced activity in the above comparison, the current catalyst can also be compared to the one used in slurry run #8862-41-46 which had 4.8% Co and Zr/Co ratio of 0.5. The high Co catalyst still showed lower activity. For example, sample 2 of the current slurry test compares to sample 3 of slurry test #8862-41-46. The specific activities were 0.054 and 0.260 mol CO/mol Co/min, respectively.

The deactivation check run showed that after 426 hours of operation bulk activity had declined from 28.5 to 17.6 mol syngas/kg. cat./hr.

(iii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ - Extended Test
Test #8862-1-31, Catalyst #8466-31

The extended slurry phase test run was begun in December 1985, continued through the Jan-Mar 1986 quarter and was concluded this quarter. Initially, the focus of the test was to demonstrate catalyst stability and to collect organic liquid samples for testing as a suitable diesel fuel. After successfully accomplishing those objectives, it was decided to attempt to obtain data from this test that could be used for kinetic studies. This section describes the operation of the slurry reactor and the tests conducted. The analytical results of the kinetic studies can be found in section 3.3. A summary of the performance data obtained during this quarter is found in Table 39 along with the results from the two prior quarters. Tables 40 - 95 list the mass balance process conditions and hydrocarbon product distributions for each sample point taken this quarter. The weight distributions for the same samples are shown graphically in Figures 18 - 45.

Using the extended test conditions of temperature = 260°C, pressure = 300 psig, space velocity = 2.0 L/g. cat./hr and CO/H₂ = 1.0 mol. ratio as the basecase, the conditions were varied as follows:

<u>CO/H₂</u> <u>(mol.ratio)</u>	<u>Space Velocity</u> <u>(L/g.cat./hr.)</u>
0.5	1.8
0.5	1.0
1.0	1.0
0.75	1.5

Subsequently, a deactivation check run was made at the basecase conditions. The bulk activity had declined from 44.2 to 38.6 mol syngas/kg. cat./hr. This was consistent with the trend line observed during the extended test portion of this slurry run, as shown in Figure 46.

Assuming that reaction rate was first order in hydrogen, a preliminary examination of the kinetics appeared to show a relationship between space velocity and kinetic rate constant. This apparent mass transfer effect was inconsistent with the impeller speed tests done earlier in this contract (see Jan to Mar 1985 Quarterly Report, pg. 17).

It was decided to repeat the impeller speed test at the basecase conditions. The impeller which had been operating at 1200 rpm since the beginning of the extended slurry test was first reduced to 800 rpm (samples 121 and 124) and then increased to 1600 rpm (sample 128). The conversion remained constant at approximately 43% with a slight deactivation over time.

A mass transfer effect should be more evident at higher conversions, so the impeller speed test was repeated one more time at the conditions which had previously shown the highest conversion. Temperature remained at 260°C, pressure at 300 psig, and the impeller speed was initially 1600 rpm. The space velocity was changed to 1.0 L/g. cat/hr and the CO/H₂ feed ratio to 0.5 (samples 131 and 134). The conversion was 67.7% (H₂ + CO). When the rpm was reduced to 800 rpm (samples 136 and 140), an approximate 3.4% drop in conversion occurred. While this is somewhat greater than the deactivation trend line, it is quite low compared to the factor of 2 change in impeller speed and does not indicate significant mass transfer effects. This reconfirms the results obtained during the first quarter.

The next test for mass transfer effects was to increase the gas velocity by increasing the nitrogen feed. (Nitrogen had been continually fed at approximately 10% of gas feed since the beginning of the extended test as a type of internal standard to aid the mass balance closure.) The total pressure would be raised simultaneously in an attempt to maintain a constant H_2 and CO partial pressure in the gas phase and hence a constant solubility in the slurry phase. Space velocity based on $H_2 + CO$ was kept at 1.0 L/g cat/hr with CO/ H_2 mol ratio of 0.5. Nitrogen was raised from 10% to 31% by volume in the feed gas. Total pressure was raised from 300 psig to 445 psig. The results are summarized below:

<u>Sample #</u>	<u>140</u>	<u>142</u>
Pressure (psig)	300	445
P(H_2) (psi)	97	95
P(CO) (psi)	58	55
Conversion (% H_2+CO)	63.9	63.5

As is evident, no significant change had occurred.

The pressure was then raised to 500 psig with no other process changes. Unfortunately, the regulator on the hydrogen cylinder was set below 500 psig, and the reactor was inadvertently operated with CO only feed. This condition persisted for the weekend until it was noticed and corrected.

Upon returning to the desired parameters, the next two samples (148 and 151) showed anomolous results with conversions of 74.3% followed by 48.9% ($H_2 + CO$).

The operating conditions were then returned to those for sample 140 which was the last sample before the elevated pressure runs. Bulk activity had declined from 28.6 to 17.4 mol. syngas/kg. cat./hr. This was well below the deactivation trend line, and it was concluded that a significant deactivation has occurred during the high pressure operation. Also noteworthy was a distinct shift in selectivity toward methane (42.7% vs 18.4%) and a reduction in the liquid fuels selectivity (22.5% vs 54.7% $C_5 - C_{23}$).

Next, the temperature was raised to 280°C for another series of kinetic experiments. Pressure was held constant at 300 psig and the other conditions varied as follows:

<u>Sample #</u>	<u>Space Velocity L/q.cat./hr.</u>	<u>CO/H₂ (mol. ratio)</u>
158	2.0	1.0
162	1.8	0.49
164	1.0	0.49
167	1.0	0.93

These high temperature runs consistently produced high methane selectivity with the highest being 56.4wt% for sample #162. Two other items to note about these were:

- 1) It was necessary to raise the reactor heat control to an unusually high temperature to maintain reactor temperature. Stabilizing the temperature had also become difficult.
- 2) The wax taps for these samples were yielding very small quantities of product. The highest calculated wax rate was 0.0018 g./min. and the average was 0.0005 g./min. This compared to 0.0267 g./min. for the last of the extended test samples (#77).

A final run was made at 280°C at the initial conditions to check for deactivation. This showed that bulk activity had declined from 36.4 to 29.9 mol. syngas/kg. cat./hr.

The last experiment was an attempt to reactivate the catalyst by running pure hydrogen through the slurry bed at 300°C and 300 psig for 66 hours. In preparation, the temperature was first reduced to 260°C and sample 173 was taken at the baseline conditions. The conversion for H₂ + CO before reactivation was 23.7%. After reactivation, the reactor was run under identical conditions and the conversion was 23.6%. Hence, no improvement was made in catalyst performance. The reactor was shut down after operating for 4417 hours with the same catalyst charge.

Upon opening the reactor after shutdown, it was discovered that the "slurry" was a powdery substance resembling catalyst only and no liquid phase. The slurry oil may have been carried over as a mist. Alternatively, the equilibrium concentration in the gas phase leaving the reactor may have been greater than the fresh wax produced at the given reaction conditions. Note that the pure hydrogen feed for reactivation could have contributed to the latter effect. It is also conceivable that some of the heavier hydrocarbons were cracked to lighter products which would increase their volatility. It is probable that the absence of a liquid phase in the reactor contributed to the temperature control problems discussed earlier, as well as to the high methane selectivities.

(d) Catalyst Characterization

The spent catalyst from the extended slurry test of the Co/Zr/SiO₂ catalyst (Test 8862-1-31) was found to contain 43.2% carbon and 2.4% hydrogen. This indicated a significant amount of coke formation, which probably occurred after the loss of slurry medium when the reactor skin temperature became excessive. This coke contributed to poor catalyst performance and could not be removed by a hydrogen treatment.

Porosity of the low surface area silica was determined and compared with that of the alumina and high surface area silica. There appeared to be no relationship between the macropore/micropore volumes and catalyst activity. The micropore volume of the alumina was between that of the silica supports, which were the two best. Catalyst activity did increase as the total pore volume of the support increased. See Table 96 for details.

Hydrogen chemisorption studies were completed on the Co/Zr/silica catalysts having higher metal loadings. The results are compared with the basecase Co/Zr/silica catalyst in the following table:

<u>Catalyst</u>	<u>B.E.T. Surface Area</u>	<u>Metal Surface Area</u>	<u>Dispersion</u>
3.5% Co/Zr/SiO ₂	316m ² /g	1.9m ² /g	6%
11.0% Co/Zr/SiO ₂	302	8.1	12%
14.4% Co/Zr/SiO ₂	145	9.3	10%

As shown, total surface area decreased as the cobalt loading was increased which correlates with the decline in activity. Metal surface areas and dispersions were enhanced at higher loadings but did not cause an increase in activity. Perhaps the higher loading catalysts could be optimized by further improvement in total and metal surface area.

3.3 Task 3 -- Slurry Reactor Kinetic Studies

The data obtained from the extended slurry test was analyzed to determine if a kinetic functionality could be established. The analysis was performed using a computer program developed for this contract that was described in the July - Sept. 1985 Quarterly Report. The available kinetic expressions were reported in Table 105 of that report and are repeated in Table 97 of this report for convenience. Except for the simple power law model, these same equations appear as formulas A-D in a recent literature article (3).

As explained previously in section 3.2 (c) (iii) a series of impeller speed tests indicated that mass transfer was not the rate limiting step. The possibility was considered that the input energy from gas expansion into the vessel was much greater than the input energy from the impeller. This would invalidate the impeller speed test. The appendix shows the calculation for the input energy from each source. Both are of the same order of magnitude. It can also be seen that doubling the rpm should have a much greater effect on mixing energy than changing gas flow rate. These calculations provided convincing evidence that the kinetic data was not obscured by mass transfer effects.

Sample points 77 to 142 were all taken at 260°C. This was the first set of kinetic data analyzed. Note that sample numbers 131 and 134 were excluded from the analysis due to both poor mass balance closure and the fact that they appeared to be aberrations when the initial attempts were undertaken to derive a kinetic expression. The data set was fit to each of the kinetic functionalities.

The first step was to account for the catalyst deactivation that had occurred during the experimental period. Fortunately, a preliminary analysis of catalyst deactivation showed it to be relatively uniform for the 260°C runs, so a linear deactivation rate was assumed. For a given kinetic rate model, the catalyst activity can be plotted against time to obtain the deactivation rate. The calculated deactivation rate can be used to adjust the reaction rate for each individual sample to a fixed point in time. The adjusted data is used in the computer model to solve for the kinetic constants. The procedure is iterative because the deactivation rate is a function of K in the rate equation and the best fit for the rate equation is dependant upon the calculated deactivation rate.

Table 98 displays the kinetic parameters derived from the non-linear regression on models 1, 2, 4 and 5. The results for model 3 are not included because it was found that the best fit for parameter K_2 in model 3 was 0. Thus, model 3 became identical to model 1 and was eliminated from further consideration. Linearized forms of the rate expressions are shown graphically in Figures 47 - 49. Note that model 5 is not presented because three rather than two constants must be determined. Figures 50 - 53 contain parity plots for each of the models, which compare the rates calculated from the kinetic expressions to those observed experimentally.

While all four of the kinetic models result in an adequate representation of the data, model 4 which includes the water inhibition effect provides the best fit. The average error of 6.2% for model 4 (see Table 98) is the smallest of the four models. Interestingly, this model has been shown by other investigators (4) to describe data with high water concentrations quite well. The low water-gas shift activity of the Co catalyst resulted in high water concentrations in these experiments. The linearized plot and parity plot for model 4 show a good fit over the entire range of data collected. The model with the second best average error was model 5. This model fit the data quite well in the mid-range but drifted at the extremes, especially at the high values of rate. Extrapolation could be a serious problem with this model.

The same procedure was followed with the five points (samples 158-171) taken at 280°C. The kinetic constants derived for model 4 were $k = 0.321$ cc/g.cat./sec. and $K = 5.30 \times 10^{-6}$ mol/cc. A plot of a linearized form of the equation is shown in Figure 54, and Figure 55 is the parity plot.

It was decided to determine an activation energy based upon the data at 260°C and 280°C. The raw k values that were calculated for the two temperatures could not be used directly because a significant drop in activity occurred during some high pressure tests performed between the samples taken at these two temperatures. However samples 153 and 155 were taken after the deactivation at the same conditions as sample 140 prior to deactivation. These points acted as a reference for the two sets of data. The calculated activation energy was 26,100 cal./g. mol.

Finally, the data taken during the stability tests at 240° was included. Since all of that data was taken at the same set of conditions, it was numerically difficult to solve

for two kinetic parameters independently. It was assumed that $K = 1.55 \times 10^{-3} \exp(-6250/RT)$ mol/cc derived from the 260°C and 280°C data was valid at 240°C. Then it was possible to solve for k ($k = 0.710$ cc/g cat/sec). In the process, a deactivation plot was derived for the entire 4400 hours of operation (Figure 57). The plot shows a fairly linear deactivation rate for each temperature. The discontinuity at around day 155 is the result of the deactivation that occurred during the high pressure tests.

An Arrhenius plot of $\ln k$ vs $1/T$ is shown in Figure 56. Unlike the previous figures which considered the beginning of a series of similar runs to be time zero, the Arrhenius plot uses the results of Figure 57 to relate all the data to fresh catalyst. The solution for k is $5.24 \times 10^9 \exp(-23254/RT)$ cc/g cat/sec. Thus, the activation energy is +23,254 cal/g mol.

3.4 Task 4 -- Fuel Product Characterization

A second sample of liquid organic product was collected from the extended slurry test of the Co/Zr/SiO₂ catalyst while running at 260°C, CO/H₂=1.0, WHSV=2.0 L/g cat/hr and 300 psig. The crude product was fractionated to obtain a diesel fuel fraction boiling between 190° and 338°C. This diesel fraction was then analyzed by E. W. Saybolt and Co. for ASTM diesel fuel specifications as shown in Table 5. There was very little difference between the samples collected at the two different test conditions. This second sample met all the requirements for the highest quality diesel fuel except for viscosity and cloud point, for which there were only small deviations from the specifications.

4.0 EXPERIMENTAL

4.1 Task 2 -- Development of Improved Supported Catalyst Compositions

(a) Catalyst Preparation

Unless otherwise noted, all catalyst preparations were carried out under a N₂ atmosphere using standard Schlenk techniques and a Vacuum Atmospheres dry box .

(i) Co₂(CO)₈/Zr(OPr)₄/SiO₂ (Catalyst #8466-58)

The silica (100.0g, Davison 952) was pretreated using the standard method. A 300-cc hexane solution containing Zr(OC₃H₇)₄.x C₃H₇OH (93.3g, 18.0g Zr) was impregnated onto the silica. After thorough mixing, the hexane was evaporated off in vacuo. A total of 74.01g of Co₂(CO)₈ (25.0g Co) was added to the modified support with 3 impregnation steps using a hexane/toluene (1:3) solvent mixture (200-cc solution volume per step). Upon removal of the solvent in vacuo, 225g of black-green catalyst was obtained, which contained 11.0% Co and 7.4% Zr.

(ii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ (Catalyst #8466-63)

This catalyst was prepared using the same procedure as the previous catalyst with the following materials:

SiO ₂	36.0g
Zr(OC ₃ H ₇) ₄ .XC ₃ H ₇ OH	67.4g, 13.0g Zr
Co ₂ (CO) ₈	53.3g, 18.0g Co

124.6g of black catalyst was obtained, which contained 14.4% Co and 10.2% Zr.

(b) Gas Phase Screening

A detailed description of the gas phase screening reactor and procedure can be found in the Project Work Plan. The catalyst charge was 10 cc for each test. Generally, only reactor temperature and CO to H₂ feed ratio were varied while pressure and space velocity were kept at 300 psig and 1000 h⁻¹ (v/v), respectively, for all the runs. Hydrogen activation was used for all the tests as follows: Hydrogen at 1000 to 3000 hr⁻¹ and 0-70 psig was passed over the catalyst as it was heated to 300°C at 3°/min and maintained there for 16 hours. The temperature was then reduced to the desired reaction temperature, CO was introduced to give 1:1 CO/H₂ at 1000 hr⁻¹ and finally the total pressure was increased to 300 psig.

(c) Slurry Reactor Tests

(i) Co₂(CO)₈/SiO₂ -- Test #8862-80-49

This catalyst was activated in the 150-cc fixed-bed, tubular reactor using pure H₂ as follows: The reactor tube was charged with catalyst in a dry box to give approximately a 110-cc bed volume and transferred to the reactor manifold sealed under N₂. The reactor was heated at 0 psig to 300°C at a rate of 1°/min with a H₂ flowrate of 1000 sccm. The temperature was maintained at 300°C for 8 hours. After cooling, the reactor was flushed with N₂, sealed and transferred to the dry box for catalyst removal. In the dry box the reduced/activated catalyst was slurried in deoxygenated Fisher paraffin oil and transferred to the slurry autoclave reactor under a N₂ purge.

For this slurry test, 80.1g of reduced catalyst in a 450-cc slurry volume was charged to the one-liter reactor giving a 17.8wt% catalyst concentration. The metal loadings before and after activation were as follows:

	<u>Fresh</u>	<u>Activated</u>
Co, wt%	4.2	4.9

(ii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ -- Test #9093-10-58

This catalyst was activated and slurried in the same manner as the previous catalyst. The reactor charge was 450-cc of a 19.6wt% slurry containing 85.7g of activated catalyst. Elemental analysis of the catalyst was as follows:

	<u>Fresh</u>	<u>Activated</u>
Co, wt%	11.0	16.4
Zr, wt%	7.4	11.5

(iii) Co₂(CO)₈/Zr(OPr)₄/SiO₂ -- Extended Test #8862-1-31

The activation and slurry charge for this test was described in the October-December 1985 Quarterly Report.

(d) Catalyst Characterization

H₂ chemisorption experiments were conducted on a Micromeritics Chemisorb 2800 using catalyst samples prereduced in the 10-cc reactor. After transfer of the samples to the chemisorption sample tubes, they were treated with H₂ at 300°C and 1 atmosphere prior to data acquisition. S. E. T. surface areas were obtained using a micromeritics Digisorb 2500. Mercury intrusion porosimetry was done using an Autopore 9200 and helium pycnometry was done using an Autopycnometer 1320.

5.0 REFERENCES

- (1) U. S. Patent # 4,499,209 to Shell Oil Company, February 12, 1985
- (2) R. L. Schneider, R. L. Howe, K. L. Walters, Inorg. Chem., 23 (1984) 4593-4599.
- (3) Deckwer, W. D., et.al., I & EC PDD, 1986, 25, 643.
- (4) Huff, G. A., and C. N. Satterfield, I & EC PDD, 1984, 23, 696.
- (5) Perry, Robert H., et.al., "Chemical Engineers Handbook" (5th edition), McGraw Hill, pp 19-7, 19-13.
- (6) Smith, J. M. and Van Ness, H. C., "Introduction to Chemical Engineering Thermodynamics" (3rd edition), McGraw Hill, p 472.

6.0 ACKNOWLEDGEMENTS

The skilled technical assistance of M. Louie and V. A. Monk is gratefully acknowledged.