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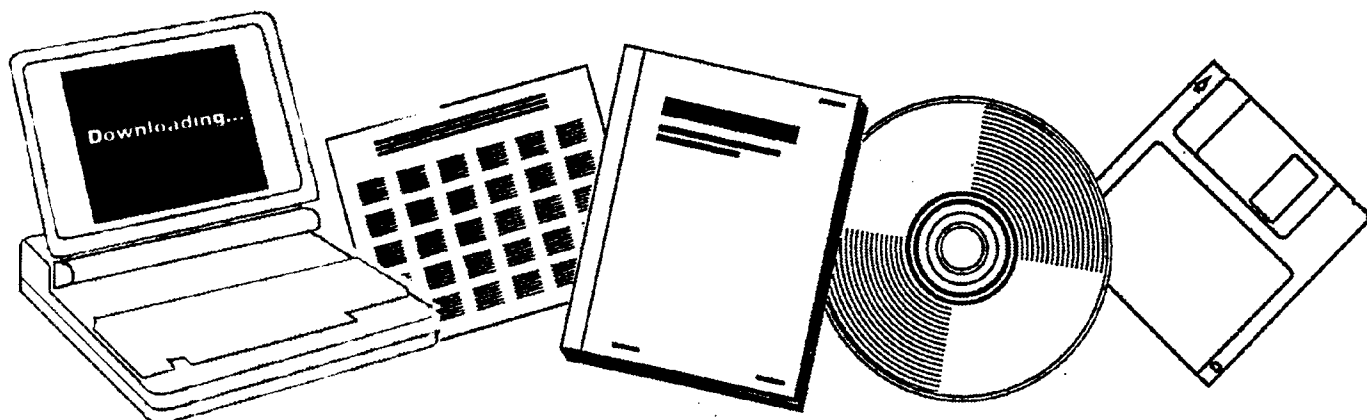
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**NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND  
PROCESS CONCEPTS FOR SELECTIVE  
TRANSPORTATION FUEL PRODUCTION. QUARTERLY  
TECHNICAL PROGRESS REPORT, 31 OCTOBER  
1984-31 DECEMBER 1984**

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

**AUG 1985**



U.S. Department of Commerce  
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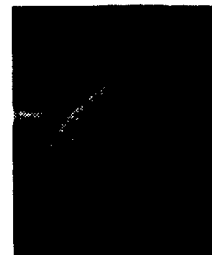
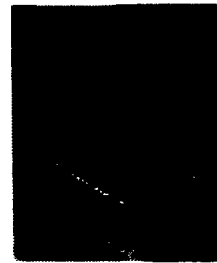
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NOVEL FISCHER-TROPSCH SLURRY CATALYSTS AND PROCESS CONCEPTS  
FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

QUARTERLY TECHNICAL PROGRESS REPORT  
31 October 1984 - 31 December 1984

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PREPARED FOR UNITED STATES DEPARTMENT OF ENERGY

UNDER CONTRACT NO. DE-AC22-84PC70030

MASTER

EAB

## EXECUTIVE SUMMARY

The first quarter objectives have been completed on 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". The detailed project work plan has been completed as Task 1 and submitted under separate cover. Task 2 work has begun and includes ten, alumina-supported catalyst preparations, nine gas phase tests and a baseline slurry run in the modified reactor. Catalyst preparation and slurry performance was demonstrated to be very reproducible.

### Task 1 -- Project Work Plan

The detailed project work plan was submitted in compliance with Task 1 of the work statement in the DOE-APCI contract "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production". The objective of this program is to develop novel improved catalysts and process concepts for the selective production of liquid transportation fuels from synthesis gas. The program will emphasize the development of highly active, selective and reproducible supported catalyst compositions. The program covers twenty-two months and is divided into four tasks. During development of the work plan, all of the equipment to be used on the project has been brought on stream and tested through shakedown runs.

### Task 2 -- Development of Improved Supported Catalyst Compositions

Catalysts prepared during the first quarter all used a gamma-alumina support. Reproducibility of catalyst preparation, i.e. metals loading, was examined by preparing four separate batches of the baseline cobalt on promoted catalyst. Different batch sizes were prepared and reproducibility was obtained by keeping the metal precursor to support mass ratio constant. Catalyst reproducibility was found to be excellent.

Several bimetallic Co/Fe catalysts were prepared either to incorporate water-gas shift activity or to improve Fischer-Tropsch activity and selectivity. None of the catalysts showed enhanced water-gas shift activity in gas phase testing. However, both Co/Fe catalysts showed high specific activities in the gas phase runs.

A slurry test of the scaled-up basecase cobalt derived catalyst was initiated this quarter. The performance of this catalyst at two temperature levels, 220 and 250°C, showed both stable activity and hydrocarbon selectivity over 102 and 220 hours on stream, respectively. The plans for the remainder of this test are to determine the role of mass transfer resistance in the overall rate of reaction and subsequently, to obtain kinetic rate data for this catalyst.

TABLE OF CONTENTS

		<u>PAGE</u>
1.0	INTRODUCTION	1
2.0	OBJECTIVE	3
3.0	RESULTS AND DISCUSSION	5
4.0	EXPERIMENTAL	6
5.0	ACKNOWLEDGEMENTS	7

## 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 solution 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. This slurry phase operation thus 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 was particularly novel in that it was prepared by supporting metal carbonyl clusters on alumina which had been modified by promoters. 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 first 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 clusters 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:

- Increasing catalyst activity
- Improving product selectivity for liquid fuels and reducing the yield of methane
- Developing catalyst systems active at high CO:H<sub>2</sub> ratios
- 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 metal 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 affect 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

This section contains potentially patentable material and has, therefore, been issued in a supplementary report marked "not for publication".

#### 4.0 EXPERIMENTAL

This section contains potentially patentable material and has, therefore, been issued in a supplementary report marked "not for publication".

5.0 ACKNOWLEDGEMENTS

The skilled technical assistance of P. A. Dotta, G. W. Long, M. Louie and L. E. Schaffer is gratefully acknowledged.

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