1.0 INTRODUCTION

The Fischer-Tropsch reaction is a fundamental component of indirect coal liquefaction. As the first step, coal or other carbon-containing solid materials are gasified to produce synthesis gas composed primarily of hydrogen and carbon monoxide. In the Fischer-Tropsch reaction, these synthesis gas components are rebuilt into a wide range of hydrocarbons, from methane to paraffinic wax (1).

The distribution of Fischer-Tropsch products can be described by the Anderson-Schulz-Flory polymerization law by which the probability of step-wise chain growth of hydrocarbons is independent of carbon number. The chain-growth probability has been shown to be a fundamental property of the catalyst and operating conditions and determines the overall product distribution (2).

In Fischer-Tropsch processing, it is possible to adjust selectivity to specific product distributions through the careful choice of catalysts and process operating conditions (3). It is generally desired to maximize the production of transportation fuels. One consequence of the Anderson-Schultz-Flory law, however, is that a wide range of products will be produced. Accordingly, the theoretical maximum yield of transportation fuel is relatively low.

If maximum gasoline yield is desired, for example, a penalty must be paid through the associated production of light ends (C_1-C_4). This type of operation is typical of Fischer-Tropsch synthesis in ebullating-bed reactors. Fixed-bed reactors, on the other hand, operate under conditions that favor the production of diesel range products. Less light ends are made because operations favor high chain growth. In this mode, however, a large fraction of waxy material is produced (C_{24}+). In either case, production of transportation fuels has associated with it the generation of a relatively large amount of less desirable by-products (Table 1.1).

Recent indirect coal liquefaction work has focused on the development of highly active Fischer-Tropsch catalysts and advanced reactor designs that minimize the production of light hydrocarbons and waxes while maximizing the production of transportation fuels (4). Significant advances continue to be made in these areas. Nevertheless, given the fundamental constraints in controlling Fischer-Tropsch product distributions, it appears likely that upgrading of Fischer-Tropsch light ends and wax by-products will remain an important consideration for indirect coal liquefaction.

Table 1.1

Fischer-Tropsch Product Distribution

Product	Wt-% Fixed-Bed	Wt-% Synthol
C_4 (Minus)	13.3	43.0
C_5-C_{11} (Gasoline)	18.0	40.0
C_{12}-C_{18} (Diesel)	14.0	7.0
C_{19}+ (Wax)	52.0	4.0
Water Soluble Chemicals	2.7	6.0

2.0 SCOPE OF WORK

The Fischer-Tropsch process is a commercially proven method of obtaining distillate product via indirect coal liquefaction. In this process, synthesis gas from a coal gasifier is converted into transportation fuel, with light gases and wax being formed as by-products. Actual yield and product characteristics are dependent on the specific Fischer-Tropsch reactor configuration and operating conditions used in the process.

The focus of the subject program was to maximize the yield of marketable transportation fuels from the Fischer-Tropsch process in a technically feasible and economic manner. With this in mind, UOP Inc. and the Engineered Materials Research Center, both wholly owned subsidiaries of Allied-Signal Inc., investigated the molecular nature of several Fischer-Tropsch by-product waxes. Processing methods were developed for upgrading and blending the light gas and wax by-products of the Fischer-Tropsch (F-T) reaction. Related program elements included an overall economic evaluation of the proposed processing schemes.

2.1 TASK DESCRIPTION

The program was split into six tasks; five of these tasks were part of the original contract while the sixth, Mobil F-T wax characterization and hydrocracking was added at a later date. Specifically, the program consisted of the following tasks:

- Task 1.0 -- Procurement of Fischer-Tropsch Material
- Task 2.0 -- Characterization of Fischer-Tropsch Waxes
- Task 3.0 -- Hydrocracking of a Commercial Fischer-Tropsch Arge Wax
- Task 4.0 -- Blending Study of Fischer-Tropsch Material
- Task 5.0 -- Economic Evaluation of the Upgrading Process Scheme
- Task 6.0 -- Characterization and Hydrocracking of a Pilot Plant Derived Mobil Fischer-Tropsch Wax

2.1.1 Procurement of Fischer-Tropsch Material (Task 1.0, Report Section 3.0)

UOP procured Fischer-Tropsch wax from a commercial Arge fixed-bed reactor product pool for use in Task 2.0: Wax Characterization, and Task 3.0: Wax Hydrocracking. Also, UOP obtained several other separated materials from the same commercial Arge reactor for use in Task 4.0: Blending Study. In addition, three low-value light cycle oils (LCO) were obtained for blending with the diesel.

Three other waxes were procured from pilot plant reactor systems for use in the subject program. The procurement effort was managed by the Project Development and Marketing groups at UOP Inc.

2.1.2 Characterization of Fischer-Tropsch Waxes (Task 2.0, Report Section 4.0)

New techniques were developed by the Allied-Signal Engineered Materials Research Center (EMRC) to provide molecular characterization of four Fischer-Tropsch reactor waxes. The sources of the reactor waxes were a commercial Arge fixed-bed reactor and three pilot plants operated by Air Products and Chemicals Inc., Union Carbide Corp. and Mobil Corp.

The Fischer-Tropsch waxes were characterized using gel permeation chromatography (GPC), high resolution mass spectrometry (HRMS), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), gas chromatography and various other physical analyses.

2.1.3 Hydrocracking of a Commercial Arge Fischer-Tropsch Wax (Task 3.0, Report Section 5.0)

UOP's HC Unibon* process, a proprietary hydrocracking technology licensed by UOP to the refinery industry, was used to upgrade the commercial Arge Fischer-Tropsch wax. Pilot plant work completed under this program at EMRC, demonstrated that catalytic hydrocracking is an excellent process for producing high quality transportation fuel from

Fischer-Tropsch wax in a relatively low severity operation. Optimum conditions for conversion of wax to diesel fuel by hydrocracking were determined in this task.

2.1.4 Blending Study of Fischer-Tropsch Material (Task 4.0, Report Section 6.0)

UOP used a proprietary Catalytic Condensation process (oligomerization) to upgrade C_3/C_6 by-products of the Fischer-Tropsch reaction to obtain a more valuable distillate product. The blending characteristics of this material, as well as those of the hydrocracked wax, with other straight-run Fischer-Tropsch synthesis products were evaluated.

Laboratory analyses were obtained for these blends and used to adjust computer-based blending correlations. Also, laboratory analyses were obtained for blends of Fischer-Tropsch products with low value refinery LCO. Corrections were made to the traditional blending correlations to account for the blending characteristics of LCO. These studies maximized the use of blending components, available from a Fischer-Tropsch upgrading complex, for production of valuable and high quality transportation fuels.

Specifically, key diesel properties such as cetane number, pour point, flash point, viscosity, API and distillation were determined for components and blends to evaluate the accuracy of normal blending correlations. All the pilot plant work, component blending and laboratory analyses were done at EMRC. The computer modeling of blend correlations and the adjustments based on laboratory analyses were performed by the Marketing Services Department at UOP Inc.

2.1.5 Economic Evaluation of the Upgrading Process Scheme (Task 5.0, Report Section 7.0)

The results of the studies outlined above were used to evaluate the overall economics of maximizing transportation fuel yield of the Fischer-Tropsch process via by-product upgrading and blending.

Wax hydrocracking using UOP's HC Unibon process was incorporated into an overall Fischer-Tropsch product upgrading complex along with other advanced processes such as catalytic condensation and the UOP CCR Platforming* process. The associated product streams were blended to yield maximum distillate. In this task, the capital and operating costs were determined and economic calculations were made to verify the feasibility of the proposed conceptual complex.

The economic analysis was performed by the Marketing Services group with necessary input from Process and Project Development, Engineering and Cost Estimating Departments at UOP Inc.

2.1.6 Characterization and Upgrading of a Pilot Plant Derived Mobil Wax (Task 6.0, Included in Report Sections 4.0 and 5.0)

The Mobil wax was produced in a two-stage Fischer-Tropsch synthesis process in a slurry reactor using a precipitated iron catalyst. This system used a low ratio H_2/CO feed gas.

The Mobil wax was characterized and upgraded using catalytic hydrocracking. The objective of this task was to demonstrate the processibility of the Mobil wax in pilot plant hydrocracking and to compare the properties and processibility to that of the commercial Arge Fischer-Tropsch wax. The operating conditions were the same as the "optimum" cases in Task 3.0: Commercial Arge Wax Hydrocracking. Also, Mobil wax is very high in iron content and techniques to remove this iron were investigated. The characterization and the hydrocracking of Mobil wax were conducted at the Allied-Signal Engineered Materials Research Center.

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