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UPGRADING OF LIGHT FISCHER-TROPSCH PRODUCTS. FINAL REPORT

UOP, INC.
DES PLAINES, IL

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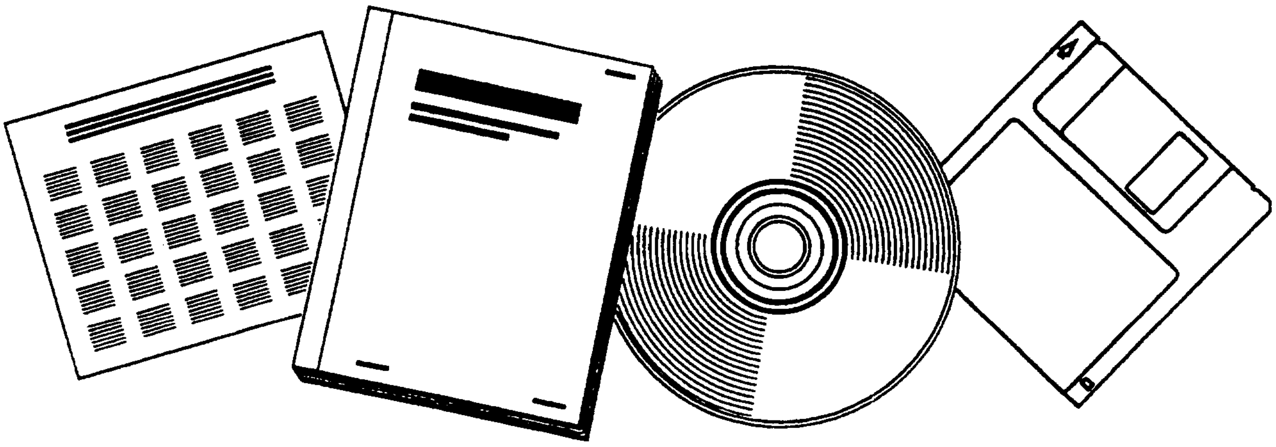

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UPGRADING OF LIGHT FISCHER-TROPSCH PRODUCTS

Final Report

By
P. P. Shah

November 30, 1990

Work Performed Under Contract No. AC22-86PC90014

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
UOP
Des Plaines, Illinois

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ABSTRACT

The upgrading of Fischer-Tropsch (F-T) light ends was studied at UOP in a program sponsored by the Pittsburgh Energy Technology Center of the U.S. Department of Energy. The goal of the program was to increase the overall yield of marketable transportation fuels from the F-T upgrading complex by focusing on liquefied petroleum gas (LPG) and naphtha. An overview of the entire light-ends program is presented in this paper. Although this contract is specifically concerned with light products (C_3-C_{11}), a separate DOE-sponsored program at UOP investigated the characterization and upgrading of the heavy end of the F-T product spectrum: F-T wax. An economic analysis of the light and heavy ends upgrading was performed to evaluate the conversion of F-T products to marketable transportation fuels.

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1.0 PRODUCT DISTRIBUTION FROM F-T REACTORS

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

The distribution of F-T products can be described by the Anderson-Schulz-Flory polymerization law, which states that the probability of the stepwise chain growth of hydrocarbons is independent of carbon number. The chain-growth probability has been shown to be a function of the F-T catalyst and operating conditions and determines the overall product distribution. [2]

In F-T processing, the selectivity to specific product distributions can be adjusted through the careful choice of catalysts and process operating conditions. [3] Maximizing the production of transportation fuels is generally desired. However, one consequence of the Anderson-Schulz-Flory law is that a wide range of products are produced. Accordingly, the theoretical maximum yield of transportation fuel is relatively low.

For example, if maximum gasoline yield is desired, a penalty must be paid through the associated production of light ends (C_1-C_4). This type of operation is typical of F-T synthesis in fluidized-bed reactors. Fixed-bed reactors operate under conditions that favor the production of diesel-range products. Fewer light ends are made because operations favor high chain growth. In the fixed-bed mode, a large fraction of waxy material is produced (C_{19}+). In either case, the production of transportation fuels generates a relatively large amount of less desirable by-products (Table 1.1). [4]

Recent indirect coal liquefaction work has focused on the development of highly active F-T catalysts and advanced reactor designs that minimize the production of light hydrocarbons and waxes and maximize the production of transportation fuels. Significant advances continue to be made in these areas. Nevertheless, given the fundamental constraints in controlling F-T product distributions, the upgrading of F-T light hydrocarbons and wax by-products is likely to remain an important consideration for indirect coal liquefaction. In 1988, UOP completed work on a DOE-sponsored program [5] in which UOP investigated the characterization and upgrading of the heavy end of the F-T product spectrum: F-T Wax (Figure 1.1). The current program focuses on the upgrading of the light F-T products (C_3-C_{11}).

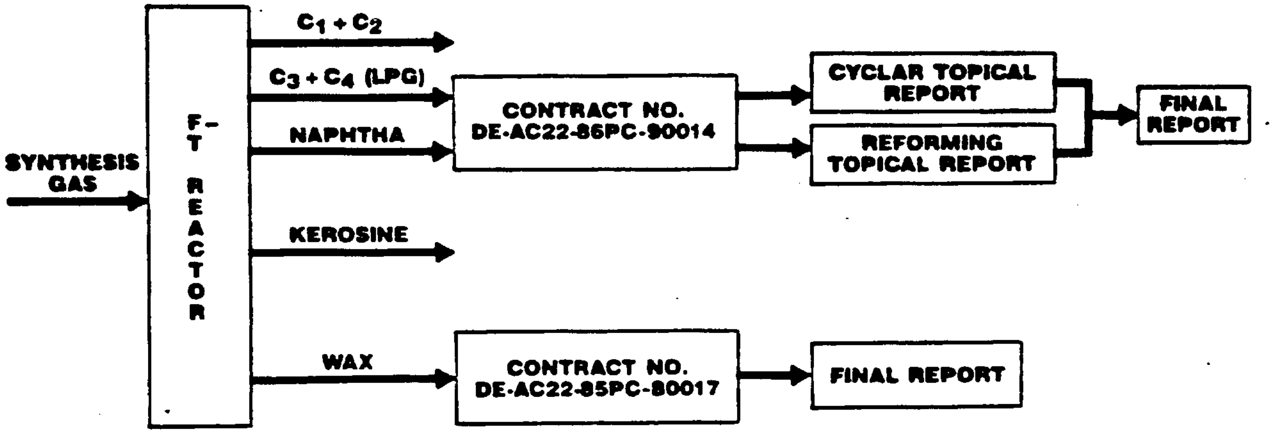
Table 1.1

F-T Reactor Selectivities

Products	Arge, wt-%	Synthol, wt-%
Methane	2.0	10.0
Ethylene	0.1	4.0
Ethane	1.8	4.0
Propylene	2.7	12.0
Propane	1.7	2.0
Butylene	3.1	9.0
Butane	1.9	2.0
C_5-C_{11} Gasoline	17.9	40.0
C_{12}-C_{18} Diesel	13.9	7.0
C_{19}-C_{23}	7.0	--
C_{24}-C_{35} Medium Wax	19.9	4.0
C_{35}+ Hard Wax	24.8	--
Water-Soluble Chemicals	3.2	6.0
	100.0	100.0

Figure 1.1

TWO CONTRACTS CONCERNING UPGRADE OF F-T PRODUCTS



2.0 NEW TECHNOLOGIES APPLIED TO LIGHT-ENDS UPGRADING

In this contract, F-T light hydrocarbons were treated as two separate species: LPG (C_3-C_5 liquefied gasses) and naphtha (C_5-C_{11} liquid product). New processes developed for the petroleum refining industry were evaluated as upgrading routes for F-T LPG and naphtha.

2.1 LPG to Aromatics via the Cyclar Process

The UOP* and BP Cyclar* process, a one-step conversion of LPG to aromatics, simultaneously increases the liquid-product yield of the F-T upgrading complex and produces a valuable coproduct: hydrogen. [6] The yield of the liquid product increases because LPG is converted to aromatics. The hydrogen coproduct may be used in hydroprocessing units within the upgrading complex or in the upstream synthesis of hydrocarbons from coal.

Aromatics also contribute to the quality of the liquid product. The aromatic Cyclar product can be used to shift the gasoline pool octane upward to a more valuable grade of gasoline or to blend with low-octane materials to further increase the size of the gasoline pool.

2.2 Naphtha Upgrading via New Reforming Technologies

Two new reforming technologies were used to upgrade the F-T naphtha into high-octane gasoline. The low-pressure CCR Platforming* process is an extension of existing commercial technology. [7] This second-generation CCR Platforming process operates at half the pressure of a typical first-generation unit to achieve higher liquid-product yield for a given product octane. A new light-naphtha Platforming* process was also used for improved liquid product yield from the C_6-C_8 portion of a full-boiling-range (FBR) naphtha.

3.0 TASK DESCRIPTIONS

The program was split into seven tasks:

Task 1. Project work plan
Task 2. Feedstock procurement and analysis
Task 3. Feedstock preparation
Task 4. Cyclar processing study
Task 5. Light-paraffin conversion study
Task 6. Low-pressure Platforming process study
Task 7. Economic evaluation

3.1 Task 1. Project Work Plan

The project work plan described the overall research program in detail. It provided the basis for monitoring and controlling the program.

3.2 Task 2. Feedstock Procurement and Analysis

The objective of this task was to procure and analyze the feedstocks to be used in the pilot plant studies. Coal-derived naphtha was obtained from a commercial F-T facility. Petroleum-derived LPG blends were used in place of LPG from a commercial F-T facility because of sample procurement and transportation difficulties.

3.3 Task 3. Feedstock Preparation

The F-T naphtha has high levels of olefins and oxygenates that must be converted prior to reforming. A two-step pilot plant hydrotreating operation was used to saturate olefins at low severity and then convert oxygenates at high severity. The initial low-severity operation avoided gum formation by the olefins. High-severity second-stage treatment reduced oxygenates to a low level to prevent water formation during reforming. The hydrotreated product was then batch fractionated into a FBR naphtha (C_5-C_{11}), a light naphtha (C_6-C_8), and a heavy naphtha (C_9-C_{11}). A minor amount of reagent-grade paraffin was blended into the FBR naphtha to achieve the desired carbon number distribution.

3.4 Task 4. Cyclar Processing Study

The use of the Cyclar process for upgrading F-T LPG was studied at UOP. [8] The Cyclar process converts LPG into aromatics.

The LPG derived from the F-T reactor is highly olefinic. Two routes for upgrading F-T LPG were investigated (Figure 3.1). In one route, olefinic LPG was fed directly to a Cyclar unit (Direct Cyclar). The alternative flow scheme used the Huels CSP complete saturation process to saturate LPG olefins upstream of the Cyclar unit (Indirect Cyclar). An 18-run pilot plant study verified that each route is technically feasible.

The LPG olefins were easily converted in the Cyclar process. Compared to paraffins, olefins result in higher liquid-product yields. This situation permits more flexibility in choosing process conditions, particularly with respect to process pressure. A significant disadvantage with olefinic feedstocks is that they can lead to excessive catalyst coking under certain conditions.

An economic evaluation procedure was designed to choose between the Direct and Indirect Cyclar options for upgrading LPG. Four cases involving three different F-T reactor technologies were defined. The main distinction among the four cases was the degree of olefinicity, which ranged between 32 and 84 wt-% of the fresh feed. In the two lower olefin cases, Direct Cyclar was preferable, but for the two higher olefin cases, Indirect Cyclar was preferable. On the basis of what has been learned in this contract, a Cyclar unit that would best fit into an F-T upgrading complex would not use complete saturation. Instead, partial saturation of the feed would be employed to take advantage of the LPG olefins without the excessive costs associated with high catalyst coking rates at olefin levels above 65 wt-%.

The Cyclar process is a promising technology for use within an F-T upgrading complex. The Cyclar process directly addresses the problem of what to do with F-T LPG. The Cyclar process uses not only C_3 and C_4 olefins, which can be polymerized as an alternative, but also C_3 and C_4 paraffins. With the exception of alkylation, which uses isobutane, few process alternatives are available for the direct conversion of LPG paraffins into liquid products.

For a 5,675 MT/d Arge upgrading complex with a wax hydrocracker operating at high severity (large LPG production rate), a Cyclar unit would contribute more than 4,500 BPSD of a high-octane (106 R+M/2), low Reid vapor pressure (RVP; 1.6 psia) aromatic product. The liquid product would be 89.1 wt-% benzene, toluene, and xylenes (BTX) aromatics and 10.9 wt-% heavier aromatics. Aside from the liquid product, the Cyclar process makes a valuable 95 vol-% purity hydrogen coproduct. The hydrogen production rate would exceed 1,200 SCFB of LPG feed, or about 14 MM SCFD. This volume of hydrogen is sufficient to change the upgrading complex from a hydrogen consumer to a net exporter of hydrogen.

3.5 Task 5. Light-Paraffin Conversion Study

The light-naphtha Platforming process is capable of converting light naphtha into a high-octane product at high liquid-volume yields. This process can make a significant contribution to light-ends upgrading. Hydrotreated F-T naphtha is extremely paraffinic, and light paraffins are the most difficult component of a FBR naphtha to reform into aromatics with traditional technology. A light naphtha (C_6-C_8) derived from an F-T reactor was used as the feedstock for this pilot plant program.

3.6 Task 6. Low-Pressure Platforming Process Study

Low-pressure (second-generation) CCR Platforming is an extension of current technology. The process pressure for the second generation is typically half that of the first generation. Significant advancements in the catalyst regenerator design have allowed this pressure reduction. Lower pressure results in higher liquid-volume yields for any given product octane.

Details of Tasks 5 and 6 have been published in a topical report. [9] The conclusion of this work was that reforming naphtha at low pressure (50 psig) rather than at high pressure (125 psig) has a significant economic advantage.

This advantage is particularly true for an extremely lean naphtha produced by F-T synthesis. For the case of a 40,000 BPSD unit processing an FBR Arge naphtha, an additional 5.4 vol-% yield is obtained at low pressure. This high yield translates into 767,000 bbl of additional reformate over the course of a year. Process economics are tightly related to liquid-product yield, and the additional reformate yield of the 50 psig operation adds more than $29,000/d to the gross margin. Although the low-pressure unit has a larger catalyst regenerator (more capital) and has a higher utility consumption, the internal rate of return (IRR) increases by a factor of 1.3 as pressure is reduced from 125 to 50 psig because of the yield advantage.

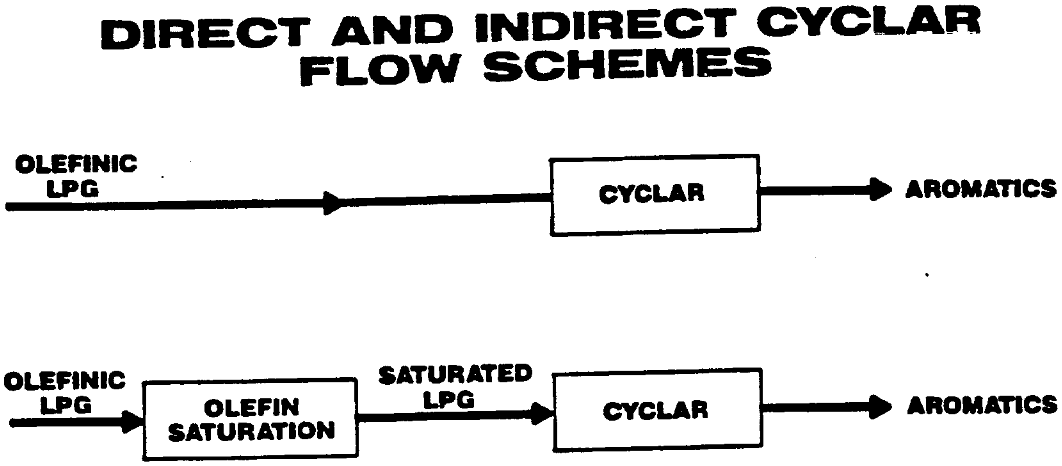
Two naphtha-upgrading flow schemes were evaluated (Figures 3.2 and 3.3). Low-pressure reforming of the FBR naphtha was compared to a split-naphtha scheme in which light and heavy naphtha was processed separately to maximize yield. For gasoline production, the study showed that the additional complexity and capital required for the split-naphtha case were not justified economically.

Finally, two sources of F-T naphtha were evaluated. Arge synthesis produces a straight-chain naphtha without aromatics. Synthol F-T synthesis produces a naphtha that is highly branched and has some aromatic content (15 wt-%). Although branched paraffins are more difficult to reform than are normal paraffins, Synthol naphtha produces more attractive reforming economics than does Arge naphtha. The economic advantage results from a lower capital-cost design (higher LHSV), which is made possible by the presence of aromatics.

3.7 Task 7. Economic Evaluation

The economic evaluation examined the overall impact of new technologies on upgrading F-T products into transportation fuels. The results of this task are described in the next section.

Figure 3.1



DIRECT AND INDIRECT CYCLAR FLOW SCHEMES

Figure 3.2

FULL-BOILING-RANGE NAPHTHA PROCESSING

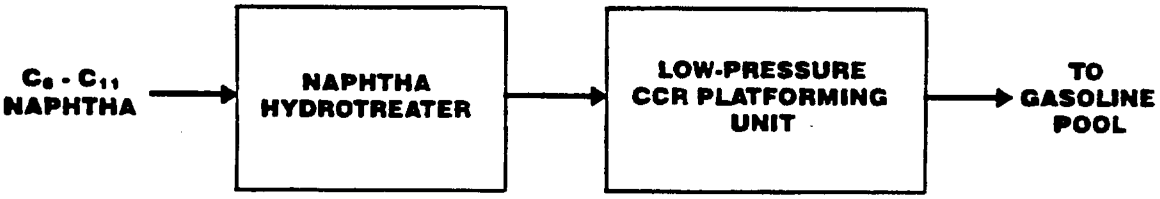
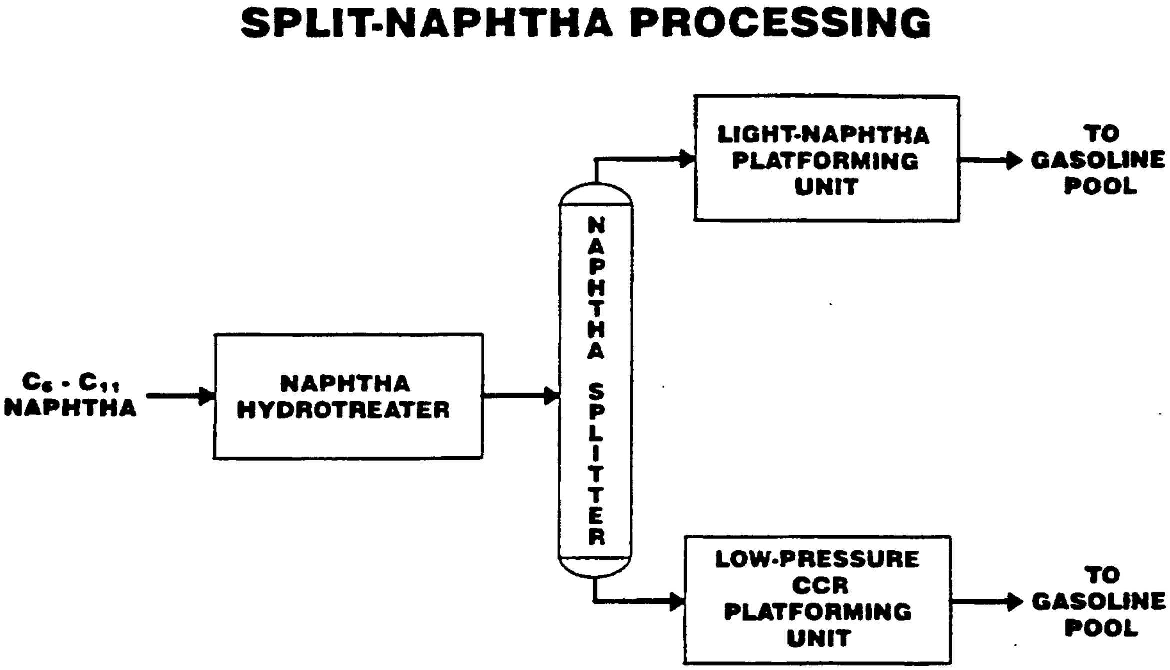


Figure 3.3


SPLIT-NAPHTHA PROCESSING
C_6 - C_{11} NAPHTHA
NAPHTHA HYDROTREATER
NAPHTHA SPLITTER
LIGHT-NAPHTHA PLATFORMING UNIT
TO GASOLINE POOL
LOW-PRESSURE CCR PLATFORMING UNIT
TO GASOLINE POOL

4.0 ECONOMICS OF UPGRADING F-T PRODUCTS

The F-T upgrading flow schemes are based on the work performed under the two UOP F-T contracts: F-T Arge wax hydrocracking and F-T light-ends upgrading. Two upgrading complexes were configured: one for Arge reactor products (Figure 4.1) and one for Synthol reactor products (Figure 4.2). The price and cost basis used in the economic evaluation is shown in Table 4.1.

A discussion on how inside battery limit (ISBL) costs are derived is given in Appendix A. The calculation procedure for the internal rate of return (IRR) is shown in Appendix B. The detailed economic analysis tabulations are given in Appendix C.

4.1 Arge Products Upgrading

The flow scheme of the Arge upgrading complex is shown in Figure 4.1. The overall complex material balance is based on 5,675.5 MT/d of Arge reactor products (Table 4.2). The gasoline and diesel pool properties are listed in Table 4.3. For the Arge case, the following process units were included in the flow scheme:

- **Cyclar Process.** The UOP Cyclar process converts the F-T LPG and LPG product from the CCR Platforming unit and the hydrocracker to aromatics. The C_6 aromatic product from the Cyclar process is sent to the UOP Alkymax* process, and the C_7+ aromatics are blended into the gasoline pool. The past work on the use of the Cyclar process to upgrade LPG was covered in the Topical Report issued under Task 3. [8]
- **Alkymax Process.** The UOP Alkymax process offers a new method of producing high-octane gasoline with reduced benzene levels. The process converts the benzene in gasoline streams into alkyl aromatics by reaction with light olefins in F-T LPG over a fixed bed of catalyst. The Alkymax process offers the opportunity to upgrade F-T LPG, increase pool octane, and simultaneously reduce benzene content. The product from the Alkymax process is added