

1.0 INTRODUCTION

The upgrading of Fischer-Tropsch (F-T) light ends was studied at UOP^R 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 the introduction, but only the "Cyclar^R Processing Study" (Task 4) is the subject of this report. Naphtha upgrading will be covered in a future report.

The introduction also covers why upgrading both light and heavy products is important within a F-T upgrading complex. Although this contract is specifically concerned with light products (C₃-C₁₁), a separate DOE-sponsored program (1) at UOP investigated the characterization and upgrading of the heavy end of the F-T product spectrum: F-T wax (Figure 1.1).

1.1 PRODUCT DISTRIBUTION FROM F-T REACTORS

The 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 rebuilt into a wide range of hydrocarbons, from methane to paraffinic wax (2).

The distribution of F-T products can be described by the Anderson-Schulz-Flory polymerization law, which states that 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 any known F-T catalyst and operating conditions and determines the overall product distribution (3).

In F-T processing, the selectivity to specific product distributions can be adjusted through the careful choice of catalysts and process operating conditions (4). 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.

If maximum gasoline yield is desired, for example, a penalty must be paid through the associated production of light ends (C₁-C₄). This type of operation is typical of F-T synthesis in fluidized-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, a large fraction of waxy material is produced (C₁₉+). In either case, the production of transportation fuels generates 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 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.

1.2 NEW TECHNOLOGIES APPLIED TO LIGHT-ENDS UPGRADING

In this contract, F-T light hydrocarbons were treated as two separate species: LPG (C₃-C₅ liquefied gasses) and naphtha (C₅-C₁₁ liquid product). New processes developed for the petroleum refining industry were evaluated as upgrading routes for LPG and naphtha.

1.2.1 LPG to Aromatics via the Cyclar Process

The Cyclar process, a one-step conversion of LPG to aromatics (5), simultaneously increases the liquid-product yield of the F-T upgrading complex and produces a valuable coproduct: hydrogen. The yield of the liquid product increases because LPG converts 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.

1.2.2 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^R process is an extension of existing commercial technology (6). 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 to improve the liquid product yield from the C₆-C₉ portion of a full boiling range naphtha. Reforming technology results will be covered in a separate topical report.

1.3 TASK DESCRIPTIONS

The program was split into seven tasks:

- Task 1.0 Project Work Plan
- Task 2.0 Feedstock Procurement and Analysis
- Task 3.0 Feedstock Preparation
- Task 4.0 Cyclar Processing Study
- Task 5.0 Light Paraffin Conversion Study

Task 6.0 Low-Pressure Platforming Process Study
Task 7.0 Economic Evaluation

Task 4, the "Cyclar Processing Study," is the topic covered in this report.

1.3.1 Task 1.0 Project Work Plan

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

1.3.2 Task 2.0 Feedstock Procurement and Analysis

The objective of this task was to procure and analyze the feedstocks 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 practicalities.

1.3.3 Task 3.0 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 hydro-treating 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 full boiling range naphtha (C₅-C₁₁), a light naphtha (C₆-C₈), and a heavy naphtha (C₉-C₁₁). A minor amount of reagent-grade paraffin was blended into the full boiling range naphtha to achieve the desired carbon number distribution.

1.3.4 Task 4.0 Cyclar Processing Study

The objective of this task was to evaluate the application of the UOP/BP Cyclar process to the upgrading to aromatics of LPG derived from F-T. The Cyclar process was developed for a paraffinic feedstock, but F-T LPG is olefinic. If Cyclar were used within an F-T upgrading complex, the olefinic feed must be sent directly to the Cyclar unit, or some or all of the feed olefins must be hydrogenated upstream of the Cyclar unit. The direct-processing option is referred to as Direct Cyclar. Indirect Cyclar processing is the alternative, using the Huels Complete Saturation Process (CSP) as the upstream hydrogenation process. The Direct and Indirect Cyclar processing schemes are depicted in Figure 1.2.

Task 4.0 is divided into three major subtasks: Huels CSP Study (4.1), Indirect Cyclar Processing (4.2), and Direct Cyclar Processing (4.3).

1.3.5 Task 5.0 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 full boiling range naphtha to reform into aromatics with traditional technology. A light naphtha (C₆-C₈) derived from F-T was used as the feedstock for this pilot plant program.

1.3.6 Task 6.0 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 the pressure reduction. Lower pressure results in higher liquid-volume yields for any given product octane.

1.3.7 Task 7.0 Economic Evaluation

The economic evaluation for this report will examine the overall impact of new technologies on upgrading F-T reactor products into transportation fuels.

TABLE 1.1

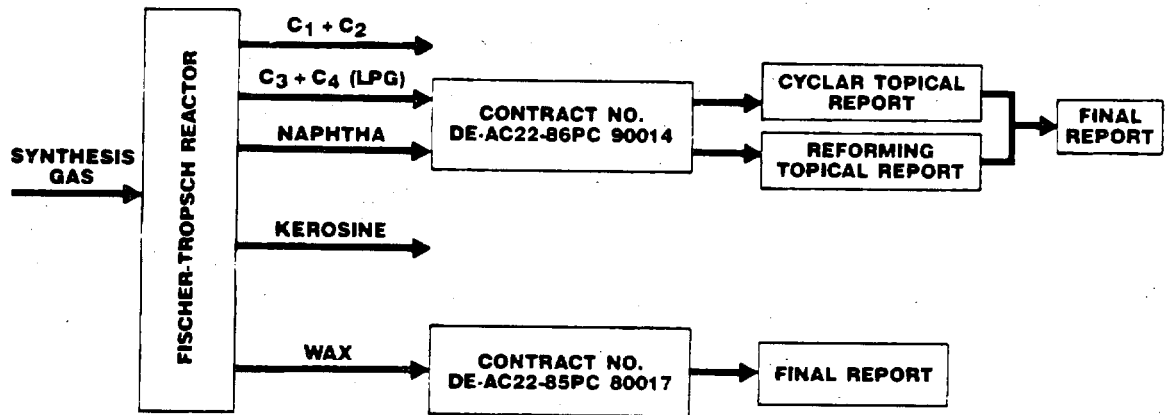
Fischer-Tropsch Product Distribution

<u>Product Distribution, wt-%</u>	<u>Arge Fixed-Bed</u>	<u>Synthol Fluidized-Bed</u>
C4- (Light Ends)	13.3	43.0
C5-C11 (Naphtha)	17.9	40.0
C12-C18 (Kerosine)	13.9	7.0
C19+ (Wax)	51.7	4.0
Water-Soluble Chemicals	<u>3.2</u>	<u>6.0</u>
	100.0	100.0

*M. E. Dry, "The Sasol Route to Fuels," Chem. Tech., pp. 744-50, December, 1982

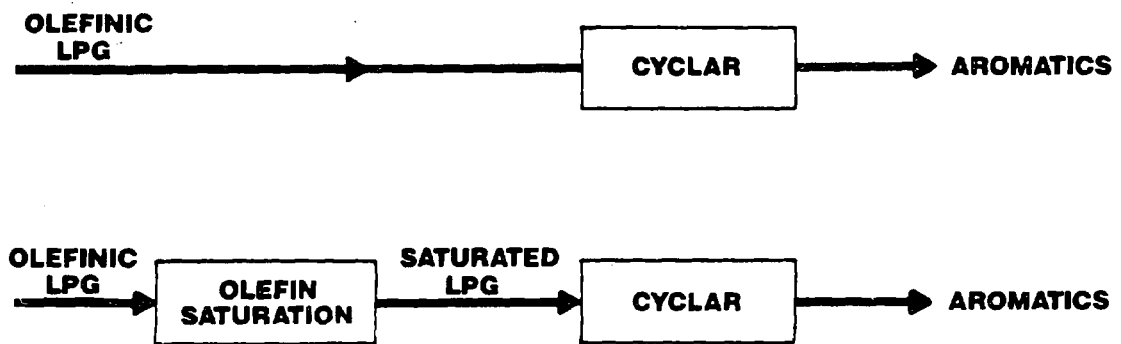
FIGURE 1.1

TWO CONTRACTS CONCERNING UPGRADE OF F-T PRODUCTS



UOP-661

FIGURE 1.2
DIRECT AND INDIRECT CYCLAR
FLOW SCHEMES



UOP 1632-13
UOP 1681-2

2.0 PROCESS DESCRIPTIONS

Process descriptions for the Huels Complete Saturation Process (CSP) and the Cyclar process are included in this section. Huels CSP has been fully commercialized. The first Cyclar process unit will be in operation in the 4th quarter of 1989.

2.1 HUELS CSP PROCESS DESCRIPTION

The Huels Complete Saturation Process (CSP) was developed and commercialized by Huels AG, Marl, Federal Republic of Germany. The process hydrogenates olefins contained in C₃-C₅ hydrocarbon streams to their corresponding paraffins. The only reaction of significance is the saturation of olefins. Skeletal isomerization, or cracking of the feed molecules, is avoided by using a high-activity catalyst capable of low-temperature operation.

The CSP feed should have less than 2-ppm sulfur and less than 1-ppm nitrogen or chloride. Drying the feed below the water saturation level is not necessary.

Two fixed-bed hydrogenation reactors are used in a typical CSP flow scheme (Figure 2.1). A recycle loop is maintained around the first reactor to control the combined-feed olefin level and thereby control the reactor temperature differential caused by the exothermic saturation reaction. Heat removed from the recycle stream by an air or water cooler provides the reactor inlet temperature control.

Fresh feed and a small excess of hydrogen relative to stoichiometric requirements are combined with the recycle stream. The effluent from the first reactor that is not recycled is sent to the second finishing reactor, where residual olefins are saturated to less than 50 ppm. Following saturation, any excess hydrogen is removed from a knockout vessel through a vent condenser.

The Huels CSP is not a complicated process, and therefore investment costs are minimal. The process requires no compressors, and carbon steel construction is used throughout. The reaction proceeds at high liquid hourly space velocity (LHSV), and so the reactor size is relatively small. Utility requirements are primarily limited to pumping and cooling costs.

2.2 CYCLAR PROCESS DESCRIPTION

This section is broken into three parts: a history of the Cyclar process development, a summary of the process chemistry, and a description of the commercial flow scheme.

2.2.1 History of the Cyclar Process

The Cyclar process is a joint development of British Petroleum (BP) and UOP. In 1975, BP began a research program to develop process technology for the conversion of LPG to more valuable and easily transported products. By 1980, a catalyst system was identified that produced high yields of aromatic-rich product from LPG. However, the process conditions required to achieve high LPG-to-aromatic selectivity resulted in rapid catalyst deactivation. Based on its experience with UOP's CCR^R regeneration technology, BP invited UOP to join the development effort. UOP adapted the BP catalyst for use in a CCR application and provided the process design and engineering for the Cyclar reactor and CCR sections. The Cyclar process was announced at the 1984 annual meeting of the National Petroleum Refiners' Association. The construction of a commercial demonstration unit is presently under way at Grangemouth, Scotland, with a scheduled start-up date in the 4th quarter of 1989.

2.2.2 Cyclar Process Chemistry

Cyclar converts LPG to aromatics in a single reaction and catalyst system. Starting from a molecule as simple as propane, the Cyclar process:

- Dehydrogenates to olefin.
- Increases carbon chain length (oligomerization).
- Promotes cyclization of the dimer or trimer.
- Dehydrogenate the unsaturated cyclic compound to the respective aromatic.

The network of Cyclar reactions is shown schematically in Figure 2.2. The formation of the unsaturated oligomer from an unreactive light paraffin is a critical step in this sequence. Although the mechanism contains some reactions that are individually exothermic, the overall sequence from LPG to aromatic product is highly endothermic. To achieve optimum conversion and selectivity, adiabatic reaction stages with interheat are employed. Five moles of hydrogen are produced for every mole of aromatic made from propane and butane. The change in hydrogen content from feed to product is greater for Cyclar processing than for naphtha reforming. The production of high-purity hydrogen as a by-product is a major benefit for this process and can help satisfy part of the large hydrogen demand of the F-T process.

The liquid product from the Cyclar process is essentially free of C₆-C₉ paraffins and naphthenes and can be used in most petrochemical conversion processes after only simple fractionation. The aromatic product is primarily BTX and has a high octane. Typical aromatics yields for pure propane and butane feedstocks are shown in Figure 2.3; corresponding hydrogen yields are shown in Figure 2.4. A Cyclar unit processing a butane feed achieves a total aromatics yield of 68.3 wt-% of fresh feed and a hydrogen yield of 5.5 wt-%, or 2,080 SCF of hydrogen per barrel of butane. Using propane as a fresh feed results in a total

aromatics yield of 64.3 wt-% and a hydrogen yield of 6.1 wt-%, or 2,040 SCF of hydrogen per barrel of propane. These Cyclar yields are higher than the yields for a BTX Platforming operation, which is presently the main source of aromatics product. The Cyclar process also eliminates the naphtha hydrotreating and solvent extraction steps normally associated with production of petrochemical-grade aromatics by naphtha reforming.

The Cyclar liquid product has attractive properties for gasoline blending. Because it is a high-purity aromatic product, it has a high octane rating. Table 2.1 shows the octanes of the C₆+ product, and also the C₇+ product obtained by fractionating the benzene. The 105.9 (R+M)/2 octane is far superior to the octane of the poly gasoline product from conventional F-T facilities. (By comparison, gasoline from a polymerization unit typically has an octane of about 87.) In addition to high octane, the Cyclar product also has a low vapor pressure and a broad distillation range (see Table 2.1), which make it a useful gasoline-blending component.

2.2.3 Cyclar Process Flow

The Cyclar process consists of two major sections: a reactor and product recovery section, which is designed to continuously produce aromatics and hydrogen from LPG, and a catalyst regeneration section, which continuously restores the catalyst to fresh activity. These sections can be operated independently at optimized conditions that benefit the overall process.

As shown in Figure 2.5, the fresh feed to the Cyclar unit is combined with a recycle stream containing unconverted feed. After being heated to the required reactor inlet temperature, this stream is converted to aromatics in a series of four reactors with interstage heating. This configuration allows high conversion despite the highly endothermic nature of the Cyclar process. The reactors are radial flow

and low pressure drop and are stacked to allow for gravity flow of catalyst between reactors. The effluent from the fourth reactor exchanges heat with the combined feed to cool and partially condense the liquid product. Liquid from the separator is recovered and fed to a stabilizer, where C₆+ aromatics are recovered as a bottoms product. Vapor from the low-pressure separator is compressed and sent to a cryogenic gas-recovery section, where hydrogen and light by-products are separated from unconverted feed components (propane and butane). The unconverted LPG is then recycled back to the reactor. Hydrogen purity of the net hydrogen stream is typically about 95 mol-%.

Figure 2.6 shows the catalyst transfer and regeneration section. Catalyst flowing from the final reactor is transferred by lift gas to the top of the regeneration tower, where it is separated from the lift gas and catalyst fines. The catalyst proceeds by gravity flow down through the regenerator. Operating conditions in the regenerator are set to fully restore catalyst performance and protect the catalyst from damage. The regenerated catalyst proceeds through transfer lines into flow control and surge hoppers and finally into the regenerator lock hopper. Lift gas then transports the catalyst back to the top of the first reactor, thus completing the catalyst circuit.

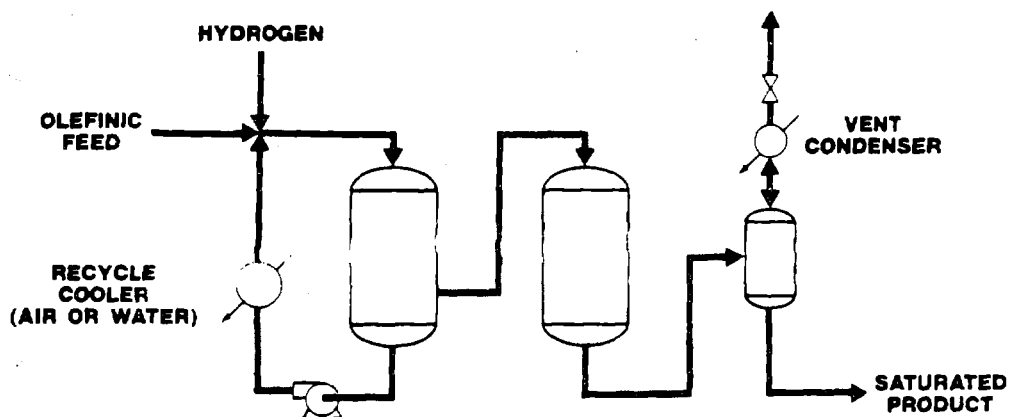
Catalyst movement is gradual, with the rate controlled at the outlet of the regeneration tower. From this control point, all catalyst transfers are regulated by level control devices. The steady movement of regenerated catalyst to the first reactor and deactivated catalyst from the fourth reactor allows a constant high level of catalyst activity to be maintained. This steady-state catalyst condition eliminates the need for changes in process temperatures to compensate for catalyst deactivation. The operation of stacked reactors with moving beds and continuous catalyst regeneration is extremely reliable, with on-stream efficiencies routinely exceeding 95%. The CCR technology is currently in place in more than 70 commercial Platforming unit installations.

TABLE 2.1

Cyclar Liquid Product Properties

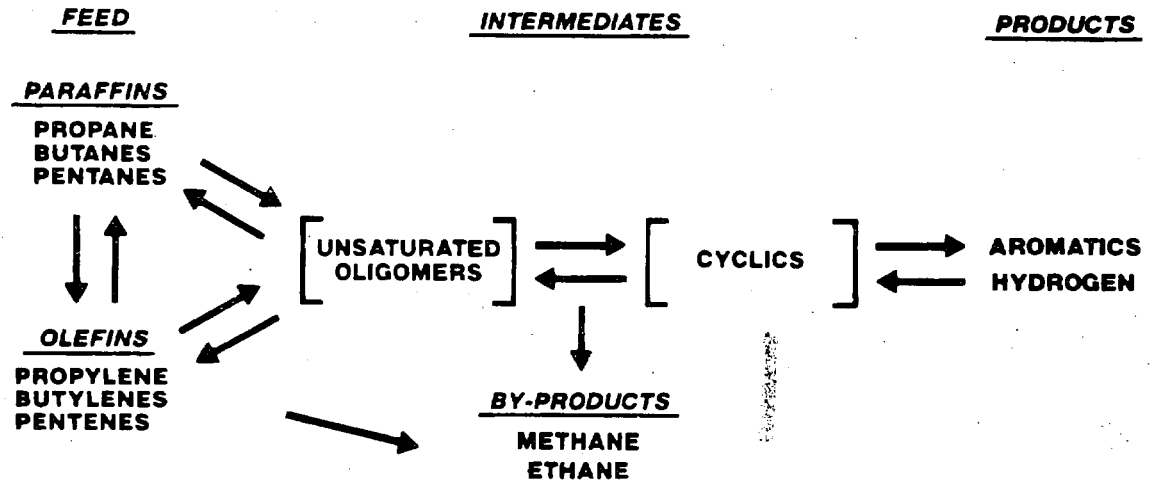
	<u>C₆+ Product</u>	<u>C₇+ Product</u>
Octanes:		
RON	111.6	113.2
MON	100.2	102.5
(R+M)/2	105.9	107.8
RVP, psia	1.6	0.7
ASTM D-86, °F		
IBP	198	223
50%	235	268
90%	295	354
EP	410	440

FIGURE 2.1
HUELS COMPLETE
SATURATION
PROCESS

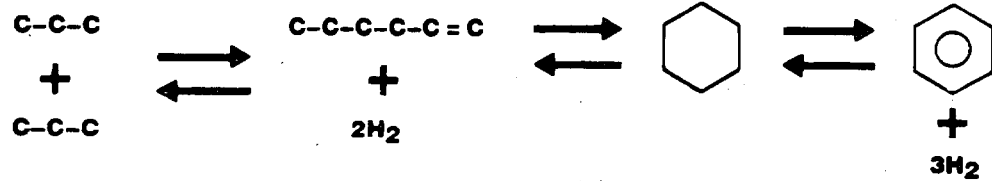


UOP 964
UOP 1512
UOP 1681

FIGURE 2.2
CYCLAR REACTION PATHWAYS

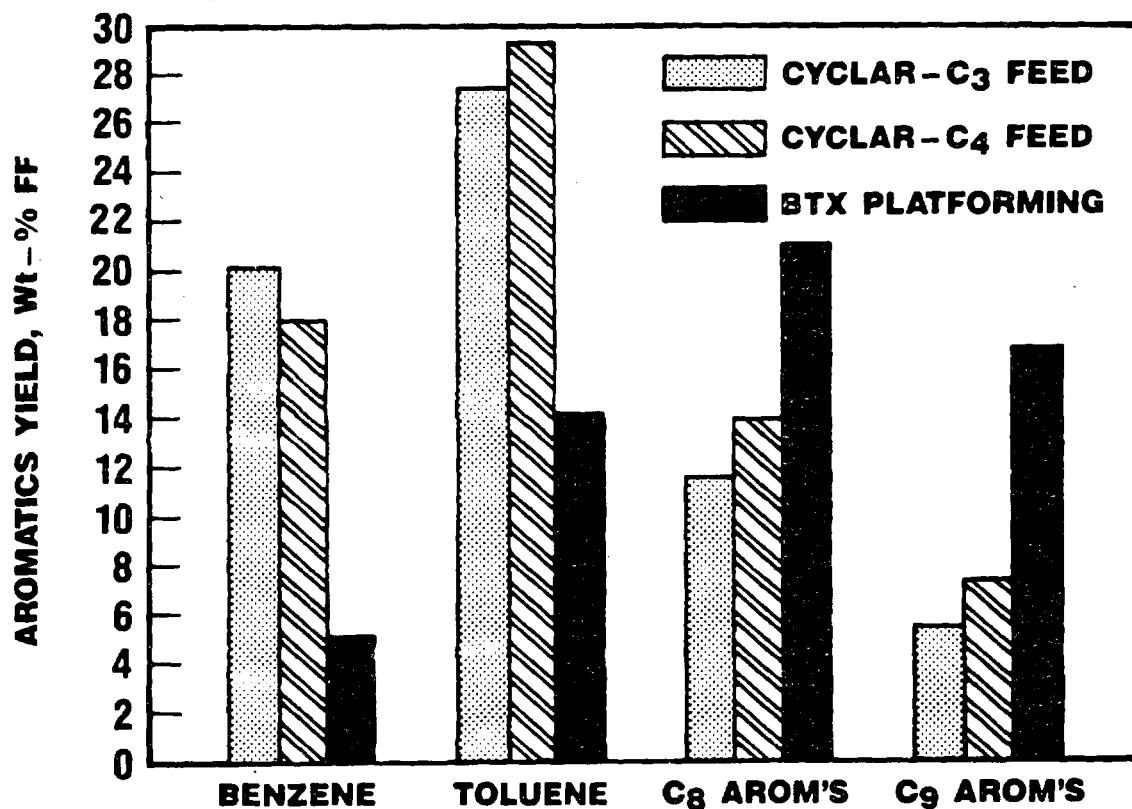


EXAMPLE FOR PROPANE



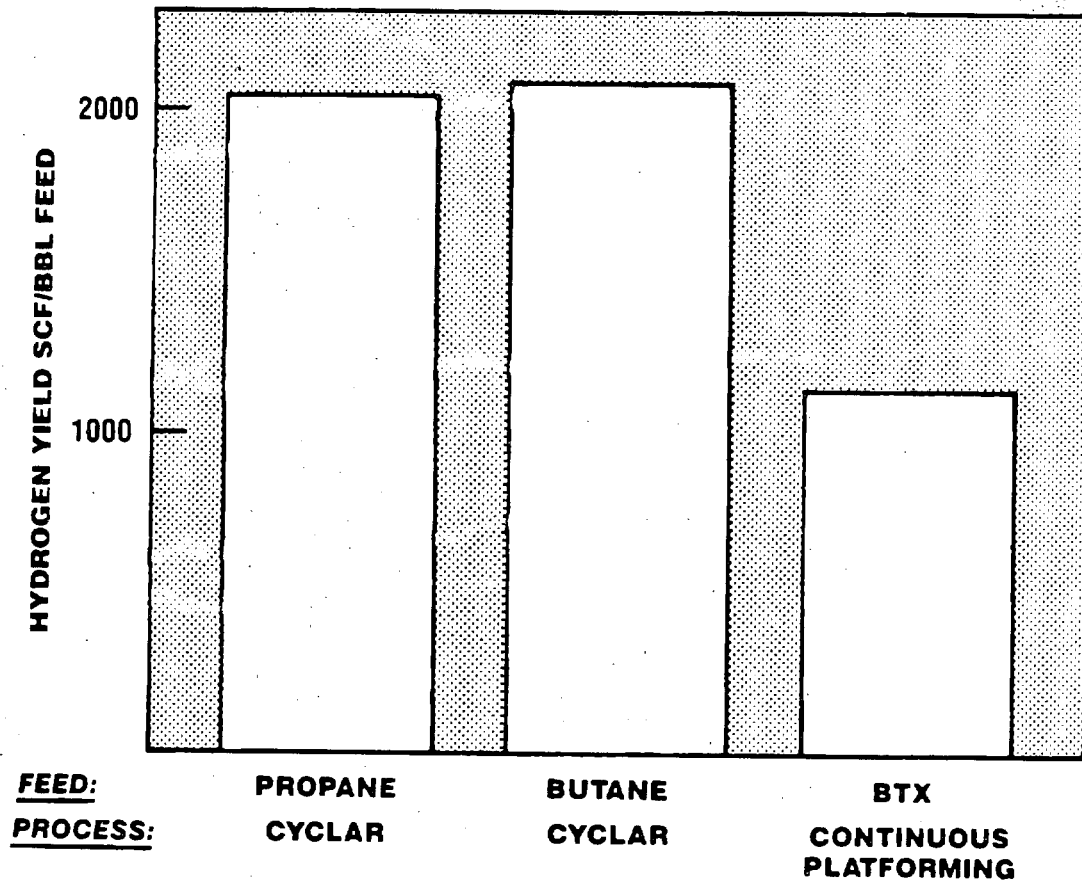
UOP 1266-2
UOP 1525F-1
UOP 1681-4

FIGURE 2.3
AROMATICS BREAKDOWN
CYCLAR vs. PLATFORMING



UOP 1544-12
 UOP 1681-5

FIGURE 2.4
HYDROGEN YIELD: CYCLAR vs.
PLATFORMING



UOP 1681-7
UOP 1544-13
UOP 1681-6

FIGURE 2.5
UOP/BP CYCLAR PROCESS FOR LPG AROMATIZATION

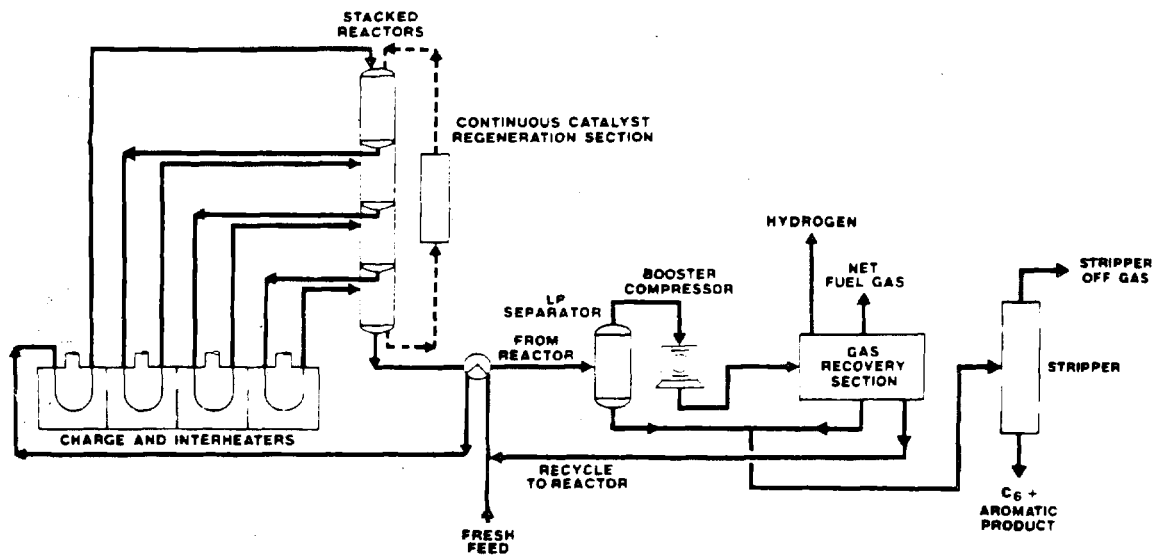
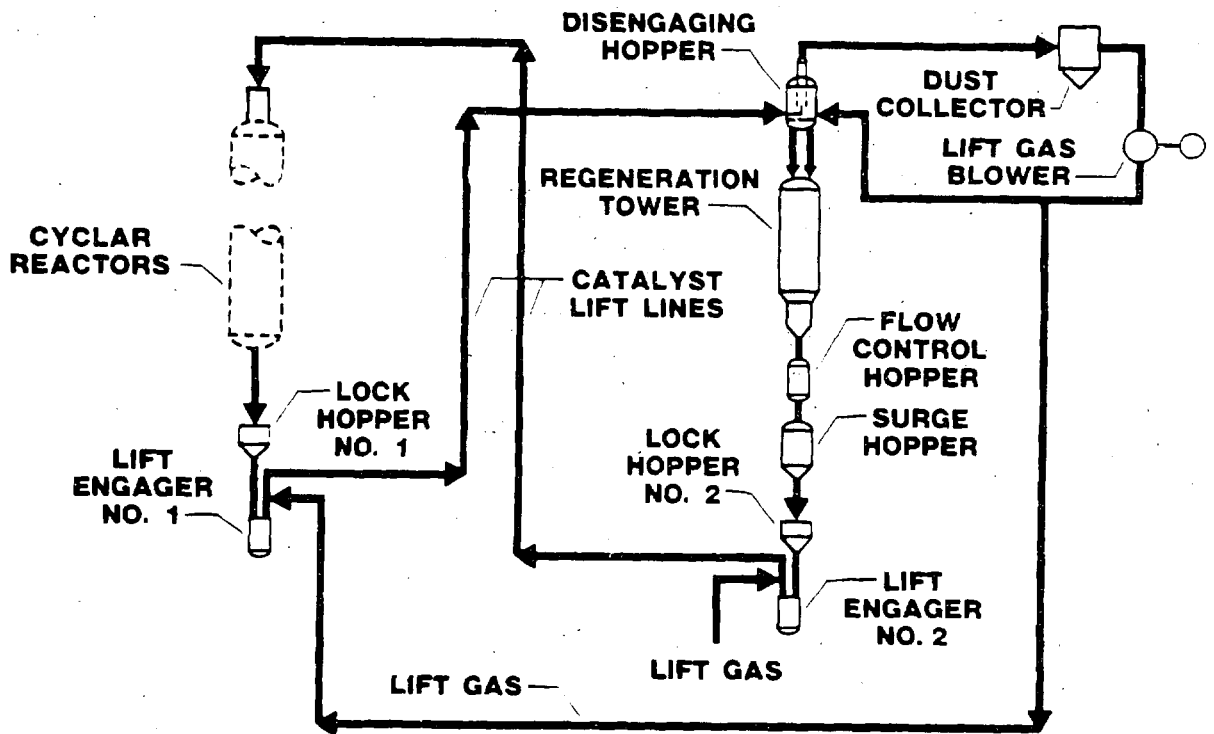


FIGURE 2.6
CYCLAR CCR SECTION



UCP 1583-11
UOP 1544-11
UOP 1581-8

3.0 PILOT PLANT DESCRIPTIONS

Two pilot plants were used to complete the Direct and Indirect Cyclar work. One pilot plant saturated LPG olefins via the Huels CSP Process. A second plant converted LPG to aromatics by the Cyclar process. A description of each pilot plant follows.

3.1 HUELS CSP PILOT PLANT

The Huels CSP process was run in a once-through pilot plant with a downflow liquid phase reactor (Figure 3.1). The LPG was charged from a nitrogen-blanketed feed-charge vessel, through a flow-rate control system, and combined with a small inlet hydrogen stream. The system pressure was high enough for all the hydrogen to dissolve in the LPG stream. Hydrogen was injected at a prespecified rate through a multiport valve connected to a timer. This technique is the same one used to inject samples in many laboratory chromatography systems.

The reactor was surrounded by electric heating elements for temperature control. Reactor effluent was collected in a product vessel and analyzed by off-line gas chromatography.

Precision balances mounted below each vessel determined the flow rates of feed and product mass. The flow rate of the hydrogen mass was calculated from the volume and pressure of the sample loop attached to the six-port valve and the sample injection frequency.

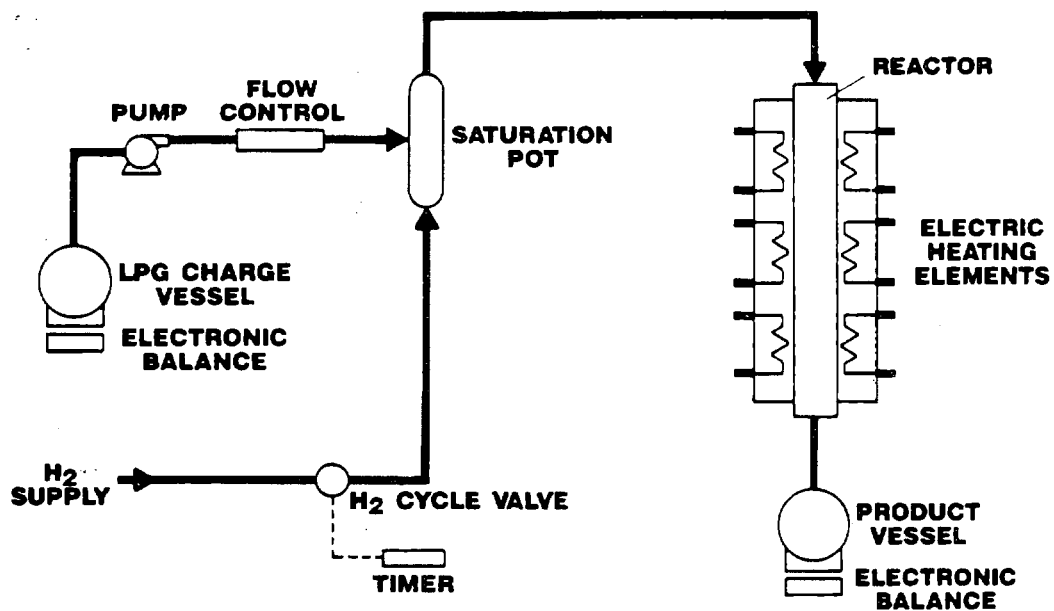
3.2 CYCLAR PILOT PLANT

The Cyclar process was run in a once-through pilot plant (Figure 3.2). The LPG feedstock was pumped from a nitrogen-blanketed vessel, through a flow-rate control system, and then charged to the reactor. An electric furnace surrounding the reactor provided the heat to drive the endothermic reaction. Aromatics produced in the reactor

were condensed in the product separator. The overhead from the separator consisted of unconverted feed, light ends, and hydrogen. The overhead gas composition was determined by on-line gas chromatography, and the volumetric flow rate of the product separator overhead was measured by a wet test meter.

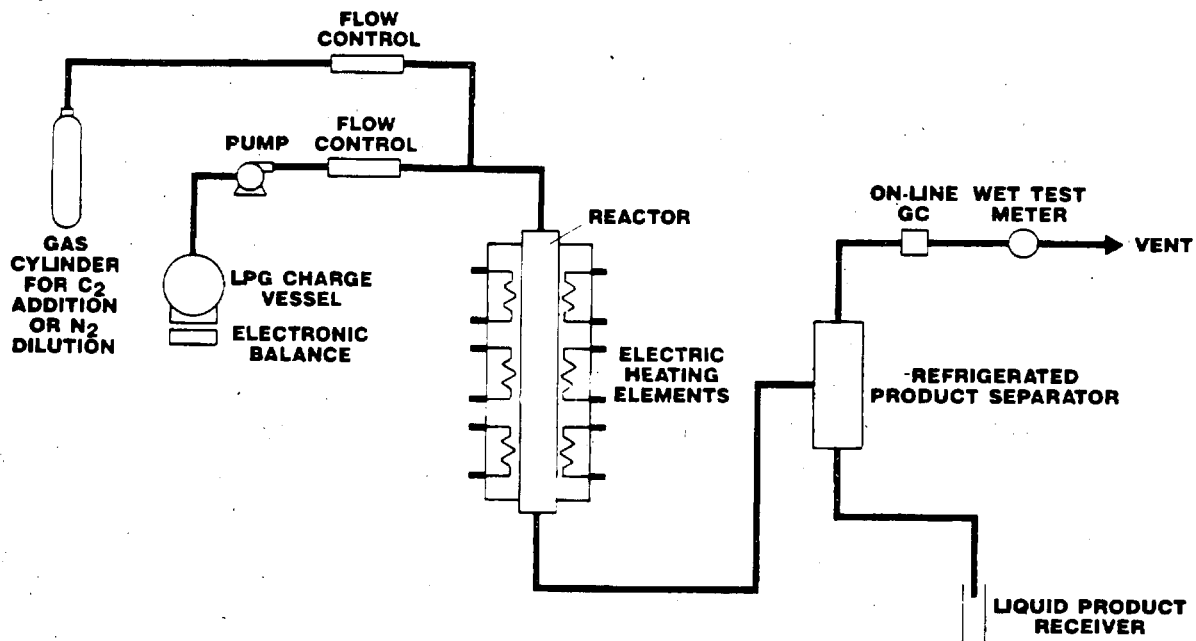
The Cyclar pilot plant mass balance was achieved by directly measuring the mass flow rate of LPG feed and aromatic product with analytical balances. The mass flow rate of the product separator overhead gas was calculated using volumetric flow measurement and gas composition analysis.

FIGURE 3.1
HUELS CSP PILOT PLANT FLOW SCHEMATIC



LOP 1581 9

FIGURE 3.2
CYCLAR PILOT PLANT FLOW SCHEMATIC



UCR 66-10