LIGHT FISCHER-TROPSCH PRODUCT UPGRADING

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INTRODUCTION

UOP and the Allied-Signal Engineered Materials Research Center have completed the second year of a Light Fischer-Tropsch Product Upgrading Program sponsored by the U.S. Department of Energy (DOE). Recent work in this program has focused on two new technologies, the Cyclar and low pressure CCR Platforming* processes, to upgrade light Fischer-Tropsch (F-T) reactor products. The Cyclar process is a one-step conversion of LPG into aromatics (1). The first commercial Cyclar unit is expected on stream in the 3rd quarter, 1989. The low pressure CCR Platforming process is an extension of existing commercial technology (2). This second generation CCR Platforming process operates at half the pressure of a typical first generation unit, achieving higher liquid product yield for a given product octane. Three second generation CCR Platforming process units are in the commercial design stage.

New technology employed within a F-T upgrading complex would impact not only the quantity and quality of desired products, but also the economics of upgrading. Different modes for implementing new technologies have been identified but the best choices are not always obvious. These decisions must be made before comparing an upgrading complex utilizing new technology versus a conventional upgrading complex. The purpose of this paper is to outline the incentives for new technologies. Alternatives for implementing new technologies are compared and an evaluation procedure that begins with pilot plant data and ends in an implementation decision is presented.

INCENTIVES AND CHOICES

A Fischer-Tropsch upgrading complex offers special opportunities to utilize new technologies. This is particularly true for upgrading F-T light ends. Fischer-Tropsch reactors produce significant quantities of LPG as well as an extremely paraffinic hydrotreated naphtha. New process technologies, soon to be commercialized, have the potential to increase transportation fuel yields from an upgrading complex. Higher yield is possible because the new technologies address specific characteristics of F-T light ends.

Upgrading Fischer-Tropsch LPG

LPG constitutes up to 25 wt-% (3,4) of Fischer-Tropsch reactor effluent (Table 1). Given the mass of this stream, a new technology that upgrades LPG into a higher value liquid product is worth considering.

Compositions of LPG produced by three F-T technologies (4,5) are given in Table 2. Each is mostly olefinic with the balance being paraffins. Cyclar process yields and product properties resulting from Arge LPG are compared (Table 3) to those expected from a conventional technology, catalytic condensation. Paraffins (propane and butane) are converted to aromatics in the Cyclar unit but are inert in the catalytic condensation process. This accounts for the Cyclar process' yield advantage. The Cyclar process produces an extremely high octane product with low vapor pressure. It also yields hydrogen, a valuable coproduct. Hydroprocessing units (hydrotreating/hydrocracking) in the upgrading complex require hydrogen as a raw material.

Two Cyclar flow schemes have been considered for upgrading F-T LPG (Figure 1). In one scheme (the "Direct" Cyclar mode), the olefinic LPG from the F-T reactor is processed directly by the Cyclar unit. In an alternative scheme (the "Indirect" Cyclar mode), the olefins are hydrogenated in the Huels Complete Saturation Process (CSP) upstream of the Cyclar unit. The saturated feed is more typical of LPG feeds for which the Cyclar process was developed.

Pilot plant studies have shown that the Direct Cyclar process is technically feasible (6). Olefins were shown to increase aromatics selectivity, but cause more rapid catalyst deactivation (via increased coking). This economic trade-off requires additional investigation before deciding on the better Cyclar mode.

Upgrading Fischer-Tropsch Naphtha

Hydrotreated Fischer-Tropsch naphthas are very paraffinic (Table 4). Paraffins are more difficult than naphthenes to reform into aromatics. Aromatic selectivities improve as pressure decreases, and lower reactor pressure is a current trend in the petroleum refining industry (2). Given the paraffinic nature of F-T naphtha, this low pressure trend is particularly important to consider for the F-T upgrading complex.

Pilot plant runs were conducted with a hydrotreated F-T naphtha at 125 psig and 60 psig. As shown in Figure 2, yields are about 5 liquid volume-% better at lower pressure over the product octane range studied. For a 25,000 barrels per stream day (BPSD) reforming unit, this yield advantage would result in over 400,000 additional barrels of liquid product in a year.

Two flow schemes involving a low pressure CCR Platforming unit are being considered (Figure 3). The low pressure Platforming unit can process hydrotreated full boiling-range (FBR) naphtha, or just the heavy portion (C_9 to C_{11}). In the split naphtha case, the light naphtha would go to a Platforming unit specifically designed to give high aromatic yields from light paraffins. Higher yields are expected in the split naphtha case, because both reforming units in this flow scheme would be tailored to the carbon range of the feedstock.

For processing F-T naphtha, a trade-off exists between a less complicated process arrangement (FBR) versus an expected increase in liquid product yield (split naphtha).

EVALUATION PROCEDURE

Trade-offs for different modes of each new technology have been identified, and it is not obvious which choices to make. The remainder of this paper describes the evaluation procedure used in this program. Information flows from the pilot plant to a commercial yield estimate and then to a capital and operating cost estimate. After these steps, an economic evaluation results in a decision (Figure 4). The choice between the Direct and Indirect Cyclar process is used as an example, but the same procedure will be used to choose between FBR and the split naphtha low-pressure Platforming process. The low pressure Platforming process results will be discussed in future publications.

Step 1: Generation of Pilot Plant Data

The results of three Indirect Cyclar (saturated fresh feed) pilot plant runs are compared (Table 5) to show the effects of process variable changes. The study was designed to bracket a range of commercial interest for liquid hourly space velocity (LHSV) and pressure. The effect of pressure and LHSV variation on conversion is evident. Increasing pressure and/or decreasing LHSV will increase conversion. Higher pressure benefits conversion (comparing Run 15 to Run 14), but aromatics and hydrogen selectivities decline. Aromatics and hydrogen yields are not very sensitive to LHSV over this interval.

Direct Cyclar (olefinic fresh feed) pilot plant runs were discussed at last year's Contractors' Review Meeting (6). Direct Cyclar demonstrates superior aromatics yield but produces more catalyst coke relative to the Indirect Cyclar (Table 6) process. The direct Cyclar process tolerates higher pressure and still maintains good aromatics selectivity (Table 7). Higher conversion is attained at higher pressure.

The Direct and Indirect Cyclar pilot plant studies provide essential qualitative and quantitative information. Pilot plant yields were obtained at a variety of reactor conditions. Also, catalyst deactivation rates and spent catalyst coke levels were measured to assist the catalyst regenerator design.

Step 2: Commercial Yield Estimation

A yield estimate makes the transition from pilot plant data to a prediction of commercial performance. Input to the commercial yield estimate includes catalyst yield, activity and stability data obtained from the design feedstock at a variety of conditions. Output from the commercial yield estimate includes combined feed definition, mass-balanced yields, a process flow sheet and catalyst requirements.

Continuous Catalyst Regeneration (CCR) technology is an integral part of the Cyclar process. The regenerator size and operating specifications depend on catalyst coking. More severe reactor conditions will produce more coke on the circulating catalyst. The catalyst must be circulated (regenerated) at a sufficiently high rate to maintain catalyst activity. Based on pilot plant spent catalyst carbon levels, the yield estimate will define a catalyst circulation rate specific for the design feedstock and process conditions. The regenerator size depends on the catalyst circulation rate and it must be designed to provide the correct environment for catalyst regeneration. The Direct Cyclar regenerator is considerably larger than the Indirect Cyclar regenerator reflecting higher coking rates associated with the olefinic feedstock.

The yield estimate is a tool for process optimization. Pressure, temperature, LHSV, unconverted feed recycle, product separator conditions, and product purification conditions can be independently varied. Indirect Cyclar feed is similar to feeds for which the process was developed, so the optimal conditions are well explored "base" conditions. For the Direct Cyclar process, a pressure exceeding base pressure was chosen to exploit higher conversion at the expense of a moderate aromatics yield decline. This significantly reduces both catalyst and compressor requirements. The catalyst inventory drops because higher conversion reduces the size of the feed recycle stream (Figure 5), so less catalyst is required on a fresh feed basis. Compressor requirements drop at elevated pressure reflecting a lower pressure differential between the product separation and the LPG recovery sections of the plant.

Step 3: Capital and Operating Cost Estimates

The yield estimate serves as the basis for preparation of the estimated erected cost (EEC). The EEC is a collection of process component costs. The major components of the Cyclar process are the reactor, charge and interheaters, compressor, LPG recovery and product purification sections. The EEC also includes detailed engineering and construction expenses (contractor fees, etc.).

The capital cost of the reactor section depends on the combined feed rate, temperature and pressure. The compressor cost is largely a function of process pressure and compressor capacity. Compressor and driver capital costs are very significant in most refinery processes and may comprise up to 25% of the EEC. Once feed recovery and product purification specifications are set, these capital costs are a function of capacity.

Offsites such as feed and product tankage are another important component of EEC. In the absence of specific information, offsite capital costs are estimated by multiplying the process unit EEC by a set factor. Offsite expenditure is typically on the order of one-third of the total EEC. If offsite expenditure is ignored, the resulting economic analysis may be misleading.

Operating costs are determined by information in the yield estimate. Catalyst consumption is related to the CCR unit circulation rate. Utility consumption is largely a function of feed conversion per pass and unit capacity. Other operating costs such as labor, maintenance, taxes, and insurance may be estimated by multiplying the process unit EEC by set factors depending on site location.

Step 4: Economic Evaluation

Capital requirements, operating costs, feedstock value and product values, are inputs to the economic evaluation. The evaluation revolves around two capital budgeting questions. First, will the timing and magnitude of operating profits justify the capital expenditure? Second, how does this expenditure compare to mutually exclusive alternatives?

Many procedures are available to assist a capital budgeting decision. Pay-back period and return on investment (ROI) are commonly used as a first approximation. Other methods such as discounted internal rate of return (IRR) and net present value (NPV) are more rigorous because they consider the time value of money and offer a clear decision rule. In this program, the discounted IRR will be used for evaluation purposes.

To determine an IRR, capital charges and operating profits (after taxes) are considered in terms of present value at unit start-up ($t = 0$). The IRR is the discount rate applied to operating profits that creates a present value of profits equal to the capital expenditure (Figure 6). The greater the IRR, the more profitable the operation. If feedstock costs and product values are known, IRR can be determined directly. If either the feedstock cost or product value is uncertain (one must be specified), the IRR can be fixed at a minimum acceptable value (hurdle rate) before solving the equation. The result indicates how low feedstock costs or how high product values must be to ensure the minimum IRR.

Sensitivity analyses are also very useful to perform. IRR can be determined over a range of LPG costs, aromatics values and hydrogen co-product values. LPG cost sensitivity is important when indirect liquefaction economics are tied into upgrading economics. Product value sensitivity is important when the aromatics from a Cyclar unit are considered as a petrochemical feedstock rather than a gasoline blending stock. Hydrogen value can range between fuel value and chemical value depending on the overall hydrogen needs of the specific upgrading complex in question.

CONCLUSIONS / PROJECT STATUS

Significant quantities of LPG and naphtha are produced by Fischer-Tropsch synthesis. New technologies are now available that would increase the yield of transportation fuels from a F-T upgrading complex by specifically addressing structural features of the F-T light ends.

Before comparing new technologies to the statuesque, decisions about how to best implement the new technologies must be made. A four-step procedure will be used in this program. Pilot plant data for each configuration are generated over a range of commercial interest with the design feedstock. Results are then used to predict commercial performance as well as to set the basis for a commercial design. Cost estimates are prepared to quantify how much capital is needed for construction and operation of each process unit. Finally, an economic evaluation is performed to evaluate under what circumstances the capital expenditure is justified.

The evaluation procedure described above is being used to choose between the Direct and Indirect Cyclar processes, and the final step is almost complete. Split naphtha and FBR naphtha low-pressure Platforming tests are in progress and the same four-step procedure will be used to choose between low-pressure Platforming alternatives.

The choice for each new technology will complete the upgrading complex pictured in Figure 7. New technology will then be compared to conventional technology (Figure 8) in terms of overall liquid product yields, product quality and upgrading economics.

ACKNOWLEDGMENTS

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TABLE 1

Fischer-Tropsch Synthesis Selectivities

	Arge Fixed Bed, Wt-%	Synthol Fluidized Bed, Wt-%	Mobil Slurry Low-Wax Case, Wt-%
Methane	2.0	10	7.5
Ethylene	0.1	4	3.0
Ethane	1.8	4	1.6
Propylene	2.7	12	8.0
Propane	1.7	2	2.0
Butene	3.1	9	6.6
Butane	1.9	2	2.1
C_5-C_{11} Gasoline	18	40	39.7
C_{12}-C_{18} Diesel	14	7	14.8
C_{19}-C_{23}	7	4	3.0
C_{24}-C_{35} Med. Wax	20		7.5
C_{35}+ Hard Wax	25		
Water Sol. Non-Acids	3	5	3.9
Water Sol. Acids	0.2	1	0.3
	100.5*	100	100.0

Note: Carbon number selectivities used directly as estimates for actual reactor effluent composition for Arge and Synthol. Published wt-% distributions are not available for these reactor products.

* As reported in the literature

TABLE 2

LPG From F-T Reactors

	Arge Fixed Bed, Wt-%	Synthol Fluidized Bed, Wt-%	Mobil Slurry Low-Wax Case, Wt-%
Propylene	28.7	48.0	42.8
Propane	18.1	8.0	10.7
Butylenes	33.0	36.0	35.3
i-Butane	1.0	3.4	0.8
n-Butane	19.2	4.6	10.4
	100.0	100.0	100.0
Total Olefins	61.7	84.0	78.1
Total Paraffins	38.3	16.0	21.9

Note: Butane i/n ratios estimated from published C_5-C_{11} data.

TABLE 3

Catalytic Condensation and Cyclar Yields

Feedstock: Arge LPG (C_3-C_4)

	Cat. Con.	Cyclar
Transportation Fuel Yield, wt-%		
Gasoline	13.0 A	65.0
Diesel	31.5	--
Gasoline Properties		
Octane (R+M)/2	87.5	105.9
RVP, psia	5.9	1.6
Unreacted LPG Paraffin Yield, wt-%	55.5	--
Fuel Gas Yield, wt-%	--	32.0
Hydrogen Yield		
H_2, wt-%	--	3.0
H_2, SCFB	--	1096

TABLE 4

Arge and Petroleum Naphtha Compositions

	F-T Naptha (Arge)*	Petroleum Naphtha (Light Arabian)
Paraffins, wt-%	100	71
Naphthenes, wt-%	0	20
Aromatics, wt-%	0	9

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* Based on composition reported in literature assuming all oxygenates and olefins are converted to paraffins during hydrotreating step.

TABLE 5

Indirect Cyclar Run Summary

Run No.	13	14	15
Pressure, psig	Base	Base	3 x Base
LHSV	Base	1.3 x Base	1.3 x Base
Rx Temp.,°C	540	540	540
Midrun Conversion, wt-%			
C_3-C_5	68.8	61.6	82.0
Selectivities, wt-%			
H_2	5.5	5.4	3.4
C_1-C_2	27.7	28.3	40.6
Benzene	19.3	18.6	14.1
Toluene	28.8	29.2	23.3
Xylenes + EB	12.7	13.1	11.1
C_9+ Aromatics	6.0	5.4	7.5
Total Aromatics	66.8	66.3	56.0

TABLE 6

Comparison of Direct and Indirect Cyclar Results

Process	Direct Cyclar	Indirect Cyclar
Run No.	3	13
Pressure, psig	Base	Base
LHSV	Base	Base
Rx Temp., °C	540	540
Midrun Conversion, wt-%		
C_3-C_5	64.2	68.8
Selectivities, wt-%		
H_2	4.1	5.5
C_1-C_2	25.1	27.7
Benzene	17.2	19.3
Toluene	30.8	28.8
Xylenes + EB	16.6	12.7
C_9+ Aromatics	6.2	6.0
Total Aromatics	70.8	66.8
Coke on Spent Catalyst, wt-%	1.0 x Base	0.7 x Base

TABLE 7

Effect of Pressure on Direct Cyclar

Run No.	3	6
Pressure, psig	Base	1.5 x Base
LHSV	Base	Base
Rx Temp., °C	540	540
Midrun Conversion, wt-%		
C_3-C_5	64.2	76.8
Selectivities, wt-%		
H_2	4.1	3.2
C_1-C_2	25.1	31.6
Benzene	17.2	16.1
Toluene	30.8	27.6
Xylenes + EB	16.6	13.8
C_9+ Aromatics	6.2	7.7
Total Aromatics	70.8	65.2
Coke on Spent Catalyst, wt-%	1.0 x Base	1.5 x Base

FIGURE 1

DIRECT AND INDIRECT CYCLAR FLOW SCHEMES

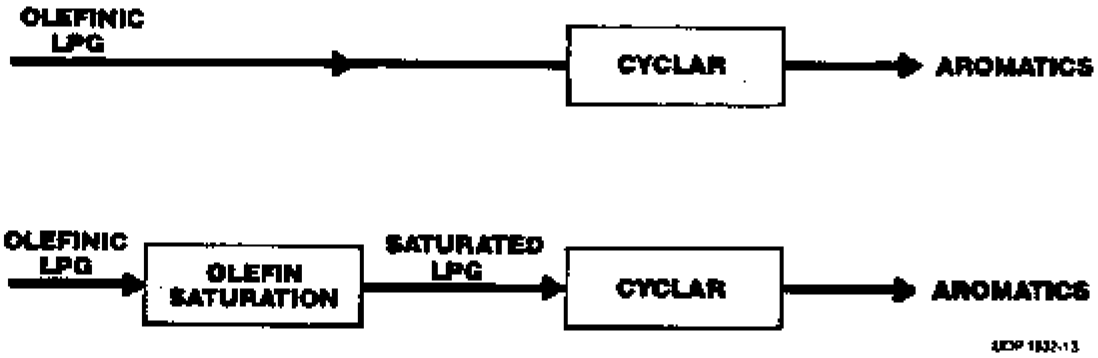

FIGURE 2

EFFECT OF PRESSURE ON LIQUID YIELDS
HEAVY F-T NAPHTHA

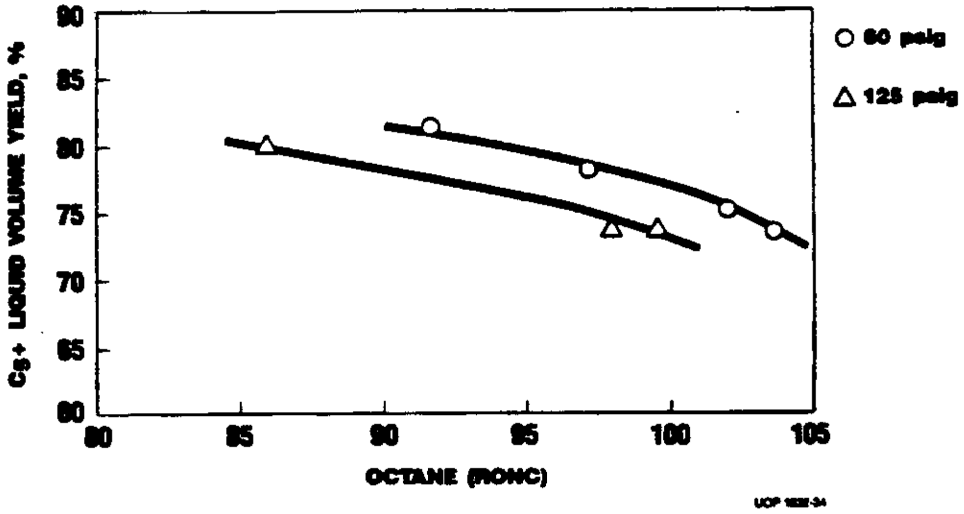

FIGURE 3

FBR AND SPLIT NAPHTHA LOW PRESSURE PLATFORMING

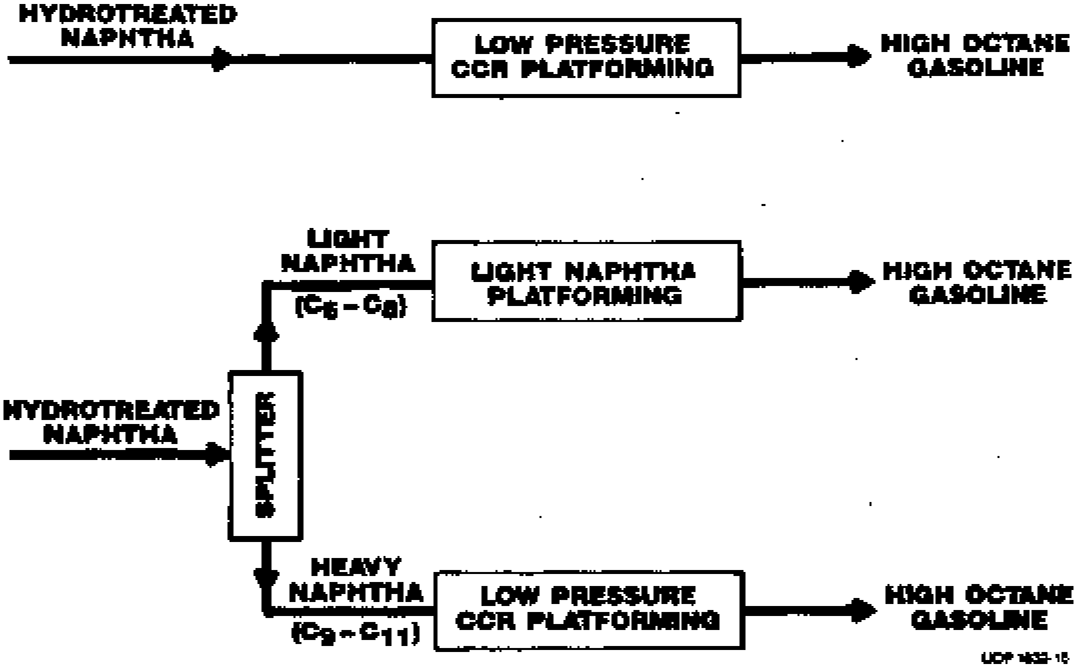

FIGURE 4

EVALUATION OF NEW TECHNOLOGY ALTERNATIVES

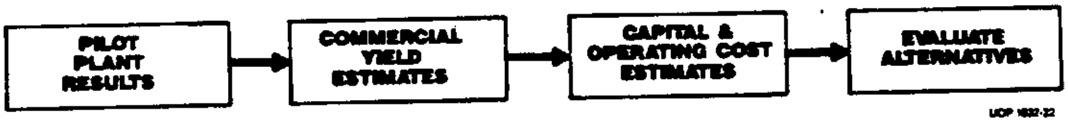

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FIGURE 5

**UOP/BP CYCLAR PROCESS
FOR LPG AROMATIZATION**

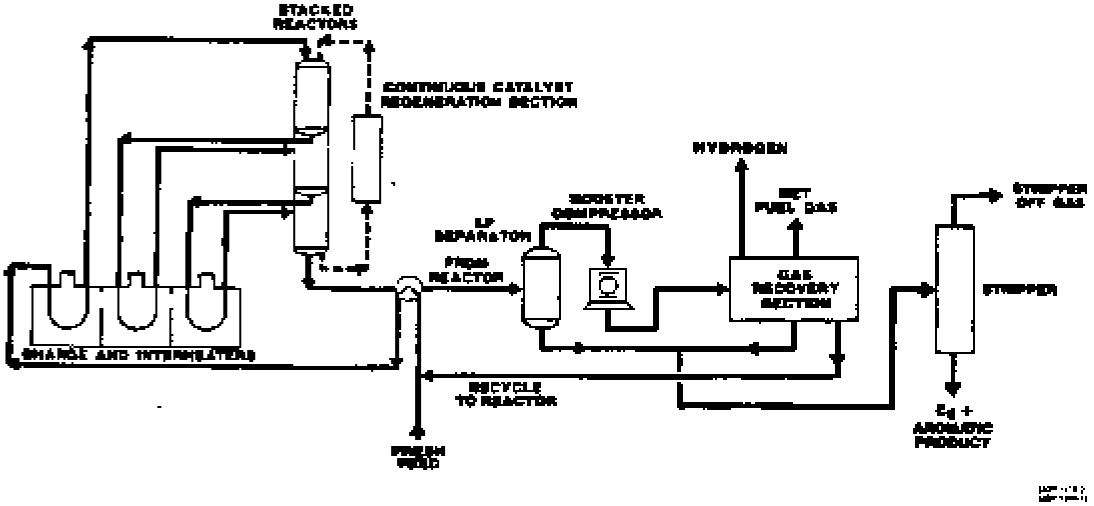

FIGURE 6

WHAT IS IRR?

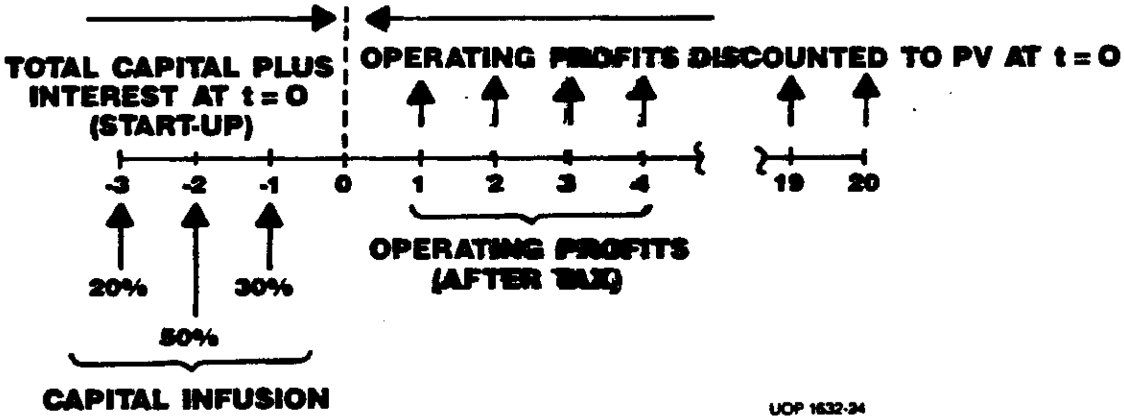

FIGURE 7

NEW TECHNOLOGY IN F-T UPGRADING COMPLEX

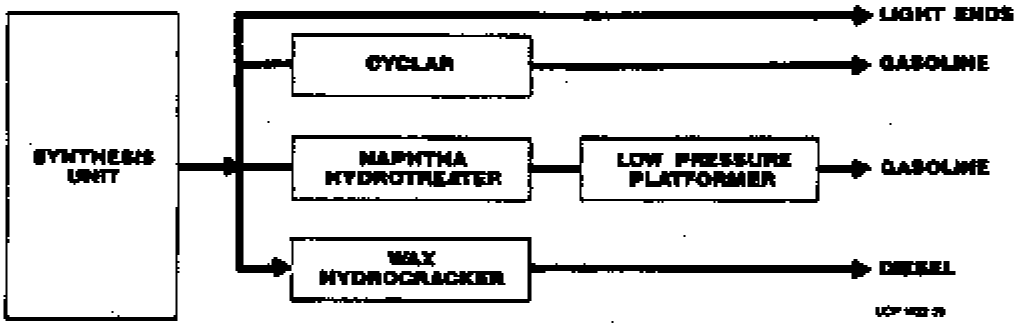

FIGURE 8

CONVENTIONAL PROCESSING