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COST EFFECTIVE ISOMERIZATION OPTIONS FOR TOMORROW'S LIGHT GASOLINE PROCESSING REQUIREMENTS

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INTRODUCTION

Light naphtha isomerization has become extremely important in recent years in helping refiners meet their gasoline pool octane demands. This is especially true for the modern UOP* Penex* and TIP* technologies because of their octane production efficiency, relatively low capital cost and overall flexibility. Today there are almost 800,000 BPSD of licensed isomerization capacity worldwide; an increase of nearly 550,000 BPSD since 1982. This surge in demand has been the result of lead phase down programs, increased sales of premium gasoline and, in some areas, proposed legislation limiting benzene content of gasoline. The addition of a light naphtha isomerization unit can result in a 1.0 to 3.0 octane improvement in the total gasoline pool, depending on feedstock and process configuration. The refiner can take advantage of this benefit by reducing reformer severity, increasing the percentage of gasoline sold as premium, or simply by meeting the requirements of unleaded gasoline.

Since 1958, UOP has been the leading licensor of light naphtha isomerization technology. This success is the result of continuous developments that have improved the efficiency and decreased the cost of isomerization. Process improvements including the once-through hydrogen Penex process, the TIP system for recycle operations, and the SafeCat* unit for sulfur removal have significantly reduced capital investment and operating costs. These improvements have been complemented by the commercialization of new catalysts including a zeolitic isomerization catalyst and chloride promoted I-8* catalyst.

Addition of light naphtha isomerization permits refiners a great deal of flexibility in running their catalytic reformers at varying severities. A reduction in reformer severity generates an increase in reformate yield resulting in increased gasoline production at constant crude rates; it also lowers the vapor pressure of the reformate, thus helping the refiner control his pool vapor pressure. Conversely, higher octane light naphtha isomerate can be combined with higher reformer severity to meet greater demands for premium unleaded products.

The refinery gasoline pool will further benefit from the addition of light naphtha isomerate with a higher front-end octane number, lower benzene content (at constant pool octane), and increased pool volume due to a density reduction of the isomerate.

This paper describes the improvements in light naphtha isomerization that have occurred over the past several years and how these improvements have allowed the refiner to meet his latest octane demands at the lowest cost.

ONCE-THROUGH PENEX PROCESS

History

UOP's Penex isomerization technology, using state-of-the-art I-8 catalyst, is the highest performing isomerization process on the market today. Ongoing developments in both catalyst and process technology have ensured superior performance and low cost light naphtha upgrading. Typical once-through isomerate octane produced with a Penex unit is 83-85 Research clear.

The use of highly active, chloride-promoted isomerization catalysts was pioneered by UOP during the mid 1960's with I-4* catalyst. Compared to prior generations of nonpromoted catalyst, I-4 allowed lower operating temperature, which favored higher equilibrium octanes. The I-8 catalyst was introduced in 1983 as an improvement over I-4 and is now used extensively in UOP Penex and Butamer* units worldwide.

I-8 catalyst offers several advantages over prior generations of isomerization catalysts, due mostly to high activity. The low temperature operation of I-8 catalyst results in very little cracking, thus producing isomerate yields close to 100 LV-%. Catalyst coking is also virtually nonexistent, resulting in extended catalyst life when poisons such as sulfur, nitrogen and water are removed from the feed. Finally, the low temperature operation produces the highest octane commercially achieved in single-pass isomerization operations.

Process Improvements

Commercial use of I-8 catalyst confirmed the ability to operate a light naphtha isomerization unit with virtually no catalyst deactivation. This exceptional performance prompted pilot plant evaluation of process changes aimed at taking advantage of this catalyst stability. These tests showed that reducing hydrogen-to-hydrocarbon ratio to levels required for stoichiometric balance had little effect on yield, octane or coking. This allowed operation on makeup gas alone, and allowed UOP to make a major modification in the Penex unit design by eliminating the need for recycle hydrogen. The new process design utilizes once-through hydrogen in a quantity just slightly above the stoichiometric hydrogen consumption required for benzene saturation. Unlike the conventional Penex flow scheme, the reactor effluent is exchanged with fresh feed and then taken directly to the product stabilizer. Comparing the new flow scheme, described in Figure 2, with the conventional design shown in Figure 1, a significant savings in equipment is realized with the elimination of:

- The Recycle Gas Compressor
- The Product Condenser
- The Product Cooler
- The Separator

The once-through hydrogen flow scheme has been in commercial service since mid 1987, with 12 new units currently in design or construction.

Penex Process Economics

The real driving force for using any process improvement is a decrease in capital and/or operating costs. As expected, elimination of equipment by employing the once-through hydrogen Penex process gives a capital savings of about 15% compared to the conventional design. Operating costs are also reduced by approximately 25% due to the reduction in hydrogen-to-hydrocarbon ratio. Table 1 summarizes the economic comparison of a recycle gas design versus once-through hydrogen operation. As can be seen, the new design allows single-pass Penex operation for as little as 10¢/octane-barrel -- a 15% savings over previous unit designs.

Liquid Recycle Options

While single-pass Penex process performance is excellent, there are instances that demand higher levels of product octane. Often this increased octane demand comes after the single-pass unit has been onstream for some time. In these cases, the low cost once-through hydrogen design can be used with normals recycle systems to achieve products in the range of 87-90 RONC. These recycle schemes can include a range of options from fractionation to liquid phase adsorption. The adsorption approach employs the UOP Molex* process unit on the Penex reactor effluent. This approach is particularly attractive for C_5 rich feeds where product octane is more greatly influenced by normal paraffin recycle than methylpentane conversion to 2,2-DMB. Fractionation of either feed or products can also be used to improve octane with a once-through hydrogen Penex design. On C_5 rich feeds, a deisopentanizer on the feed provides benefits in Penex cost and product octane while C_6 rich feeds support a deisohexanizer on the product streams. UOP can optimize the selection of fractionation and sieve based recycle to ensure optimum octane performance and unit cost.

THE TOTAL ISOMERIZATION PROCESS

History

The TIP system was developed in the early 1970's as a way of economically breaking the equilibrium octane barrier. At the higher temperature operating conditions for zeolitic catalysts, thermodynamic equilibria limit the amount of octane upgrading that can be achieved with a typical light naphtha to about 79-80 Research clear. A TIP unit overcomes the thermodynamic limitation by recovering and recycling virtually all unreacted low octane normal paraffins leaving the isomerization reactor. By separating and recycling to extinction the normal paraffins in the reactor effluent it is possible to exceed thermodynamic equilibria and produce isomerate octane in the range of 87-90 Research clear. Molecular sieve technology is the most economical means of selectively separating normal paraffins from a mixture of paraffins, naphthenes and aromatics.

The TIP unit is a highly efficient integration of UOP's vapor phase naphtha IsoSiv* adsorption technology for the separation and recovery of normal paraffins with UOP's zeolitic isomerization process for hydroisomerization of C_5/C_6's. Extensive integration, made possible by similar operating conditions such as pressure, temperature and environment, reduces the overall cost of the process. Figure 3 presents a typical TIP flow scheme.

The key to the high efficiency and operating flexibility of the TIP system is the rugged molecular sieve adsorbent and platinum loaded zeolite catalyst, which are resistant to impurities normally present in C_5/C_6 feedstocks. Because the zeolitic catalyst and adsorbent are resistant to sulfur and water compounds, there is no need for separate feed and makeup hydrogen pretreatment or special operator attention. Both the catalyst and adsorbent can withstand upsets in operating conditions without permanent loss of activity or capacity and are regenerable, either in situ or ex situ, when coked due to a major process upset. Refiners have experience with zeolitic catalysts in catalytic cracking and hydrocracking and are familiar with their ruggedness, stability, ease of operation and regeneration. Both the catalyst and adsorbent used in the TIP unit are manufactured by UOP, thus assuring the user that this durability and consistent high quality are maintained.

Process Improvements

Over the years development work has continued to improve TIP technology. Because the hydrogen recycle loop is a major point of integration of the isomerization and normal-paraffin recycle sections of the TIP unit, the quality of the recycle gas has a strong influence on the capital and operating costs. The integration of a Polybed* PSA hydrogen purifier into the makeup stream of the TIP unit represents a significant improvement in the cost of light naphtha total isomerization. The use of the hydrogen purifier reduces flow rates and equipment sizes, improves adsorbent stripping efficiency, lowers operating pressure requirements and protects the TIP unit from potentially damaging impurities, which may be present in the makeup stream.

Additional process improvements, coupled with improvements in the zeolitic catalyst have resulted in a significant reduction in catalyst requirements, elimination of a troublesome refrigeration unit, lowered adsorbent requirements and improved heat integration.

TIP System Economics

As a result, today's TIP unit produces 87-90 Research octane isomerate for as little as 18.0¢/octane-barrel. This is a 30% drop in octane- barrel cost since 1983. Table 2 compares the octane upgrading cost for a circa 1983 TIP unit with today's modern TIP processing hydrotreated Light Arabian LSR.

PROCESSING SULFUR CONTAINING FEEDSTOCKS

More than half the refineries in the world do not presently hydrotreat the C_5/C_6 fraction of the gasoline pool. In the past, it was necessary to build a new hydrotreater to achieve optimum isomerization performance with such feeds. UOP's SafeCat process offers a lower cost alternative. The SafeCat process is a modular process, which closely integrates with the TIP unit as characterized in Figure 4, to provide sulfur free performance at approximately one-half the cost of a new hydrotreater.

The SafeCat system enables the isomerization reactor to operate in a sulfur free environment, thus maintaining full catalyst activity and providing maximum octane boost. The SafeCat process is the result of extensive pilot plant testing and was commercialized in March 1987. In addition to processing up to 400 wt-ppm sulfur in the fresh feed, the SafeCat unit also removes water and nitrogen contaminants.

Table 3 shows the comparison between two TIP units processing a sulfur bearing feed. In the base case a conventional hydrotreater is used to desulfurize the feedstock. As an alternative the SafeCat process is employed to provide the same degree of desulfurization. As can be seen in Table 3, the SafeCat system saves the refiner 15% in capital cost and another 35% in utility cost.

INCREASED OCTANE PRODUCTION VIA C_5/C_6 ISOMERIZATION

As the clear octane number of the gasoline pool increases due to lead phase down or market shifts towards increased sales of premium fuels, refiners are critically looking at the ability of their existing processes to produce the required incremental octane. While the ability of existing equipment to produce the incremental octane is important, the cost of octane production via these avenues is equally, if not more, important.

As previously discussed, modern Penex C_5/C_6 isomerization technology can upgrade hydrotreated light naphtha to a product octane of 83-85 Research clear at a cost as low as 10¢/octane-barrel. With the TIP/SafeCat technology, sulfur containing light naphtha can be upgraded to a product octane of 87-90 Research clear for a cost of approximately 20¢/octane-barrel. These costs must be compared to those from other octane sources in the refinery. In reality, the only unit with substantial octane flexibility and pool impact is the catalytic reformer.

The cost of octane production via catalytic reforming is a function of a number of variables, including:

- Octane severity
- Reactor pressure
- Feedstock quality (PONA and distillation)
- Hydrogen and light ends credits
- Downtime and regeneration expenses (fixed-bed units)
- Treatment of capital

The complexity of this variable list prevents a rigorous calculation of reformer upgrading costs. It can qualitatively be said, however, that as reformer severity is increased, while holding the other variables constant, the octane production cost will necessarily increase due to increasing C_5+ yield loss. In the case of fixed-bed reformers, reduced on-stream efficiency and increased regeneration expenses will also increase reforming costs.

Some reformers have actual limits on octane production because of space velocity and reactor temperature constraints, while other units may have only economic limitations. In the former case, C_5/C_6 isomerization may be the only solution short of outside MTBE/toluene purchases; while in the latter case, light naphtha isomerization is generally a more cost effective solution relative to incremental reformer severity.

Case Study

To illustrate the advantages of adding light naphtha isomerization, case studies have been developed showing the effect of C_5/C_6 isomerization on reformer severity and overall pool yield when producing an 87 (R+M)/2 "regular" clear pool and a premium 89 (R+M)/2 clear pool.

The basis for these case studies is an integrated FCC refinery processing 100,000 BPSD of Arabian Light crude. Gasoline pool components are light straight run naphtha, reformate, FCC gasoline, alkylate, poly gasoline and optional MTBE purchase. The reformer in the case study is a 300 psig semi-regenerative unit operating with high performance Pt/Re catalyst. A gasoline RVP specification of 9.0 psi is set for all cases. Table 7 provides the basis for each flow and previous unit cost calculations.

Regular Pool -- 87 (R+M)/2 Clear

The base case gasoline pool blend is shown in Table 4. The straight run light naphtha is blended directly into the pool and a reformer severity of 96.5 Research clear octane is required to meet pool octane specification of 87 (R+M)/2. The blended gasoline yield is 48,282 BPSD or 48.3 LV-% of crude.

The addition of a single-pass Penex unit boosts the octane of the light naphtha to 84.5 RON (82.5 MON) and allows a reduction in reformer severity to 91.2 RON clear. Reformate yield increases by 5.0 LV-%. Butane addition to the pool can be increased because of a decrease in reformate RVP, and the overall gasoline yield increases by 1,018 BPSD to 49,300 BPSD. A gross revenue increase of approximately 3.2 MM/year is realized after adjusting the incremental gasoline production for hydrogen and light ends credits.

Premium Pool -- 89 (R+M)/2 Clear

The economic attractiveness of C_5/C_6 isomerization relative to other options increases as pool octane requirements increase. To achieve the 89 clear pool octane without C_5/C_6 upgrading requires the use of MTBE due to a constrained high pressure reformer operation. Two alternative approaches can be considered:

1. Add MTBE to the 87 pool operation to increase pool octane without a reformer change.

2. Increase reformer severity from 96.5 to 100 RON clear operation to limit MTBE addition to 2500 BPSD or about 5% of the pool.

Addition of MTBE as described in alternative (1) is a costly operation. Table 5 shows the change in pool composition to achieve an 89 (R+M)/2 clear octane while maintaining reformer severity at 96.5 RON clear and adding MTBE. As can be seen, this requires addition of 4598 BPSD MTBE at a current price of 80¢ per gallon. This results in an additional expense of almost 51 MM$/year, or an incremental upgrading cost of almost 31¢/octane-bbl. While this is certainly a viable option, it is certainly more expensive than the 10-20¢/octane-bbl upgrading cost seen with light naphtha isomerization, and may be less attractive due to limited supplies of MTBE.

Alternative (2) is a more realistic approach for this refining situation and will, thus, form the basis for comparing the effects of adding C_5/C_6 upgrading to attain an 89 pool octane. In this alternative some MTBE has been added along with a reformer severity increase to 100 RON clear to achieve 89 pool without LSR isomerization. The pool composition for this case is shown in Table 6.

The addition of light naphtha isomerization will greatly improve the economics of this operation because of both the high reformer severity and the expensive MTBE purchase. This upgrading can be achieved by several different routes. As shown in the previous example, a single-pass Penex could be employed to increase C_5/C_6 octane and reduce reformer severity while maintaining pool octane levels. The Penex process concept could be extended for maximum efficiency by the addition of a low-octane component recycle to achieve maximum octane boost in the C_5/C_6 stream.

If the light naphtha contains sulfur, the most cost effective upgrading scheme is integrated TIP and SafeCat units. Addition of a TIP/SafeCat unit producing an 88 RON (85.9 MON) product allows a decrease in reformer severity, and possibly elimination of MTBE while still meeting the 89 (R+M)/2 pool requirement. Two possible approaches could be taken to most effectively use the benefits of C_5C_6 upgrading depending on the particular refinery needs. First, MTBE purchase could be maintained while drastically reducing reformer severity. In this case adding 88 RON isomerate, while maintaining the 2500 BPSD MTBE purchase, allows reduction of reformer severity from 100 RONC to 93 RONC. This decreased severity increases gasoline pool yield to 51,428 BPSD, or 51.4 LV-% of crude. The incremental gross revenue of this case after product credits is over 7.5 MM$/year.

Another possible approach would be to just slightly decrease reformer severity from 100 RONC to 96.5 RONC, and completely eliminate MTBE purchase. While this case reduces the pool yield due to removal of MTBE, the credit gained from eliminating the MTBE purchase improves cash flow by ~11.0 MM$/year while increasing pool octane to 89 (R+M)/2 clear.

Compared to the first case, it can clearly be seen that higher pool octane demands provide better opportunities for application of light naphtha upgrading. Use of C_5/C_6 upgrading can also enhance the options available in terms of reformer severity, MTBE purchase and ultimate pool octane. The actual route used for isomerization requires optimization for each refinery situation.

RE-EVALUATE ISOMERIZATION ECONOMICS

As clear pool octane levels have increased, requiring increased reformer severity and MTBE purchase, octane production costs have increased significantly. Low cost light naphtha isomerization is now even more important in avoiding high reformer severity, maintaining low octane production costs, and maximizing overall refinery profitability. Decisions made in the past favoring other means of octane enhancement may have been appropriate based on limited capital availability and moderate octane demand. These strategies should now be reconsidered in light of increasing pool octane demand and decreasing isomerization costs.

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* UOP, Penex, TIP, I-8, SafeCat, I-4, IsoSiv, Polybed, Butamer and Molex are trademarks and/or service marks of UOP.

TABLE 1

Recycle Gas vs. Once-Through Hydrogen Penex

Economics (1)

Case	Once-Thru Hydrogen	Recycle Gas
Erected Cost, MM$	5.5	6.4
Operating Cost, $/D		
Utilities	1682	2242
Chemical/Consumption	4449	4449
Catalyst	1772	1772
Yield Loss	2194	2194
RVP Debit	1003	1003
Fixed Charges	8461	9224
Product Credits, $/D		
(Fuel Gas)	(4058)	(3161)
(LPG)	(2818)	(2818)
Product Upgrade (Octane-bbl/D)	123,796	123,796
Processing Cost, ¢/Oct-bbl	10.2	12.0

(1) See Table 7 for Basis.

TABLE 2

TIP Design Improvements

Economics (1)

Case	First Generation TIP	Current TIP
Erected Cost, MM$	17.0	11.3
Operating Cost, $/D		
Utilities	6455	5982
Chemical/Consumption	5548	4894
Catalyst	962	739
Yield Loss	8874	5865
RVP Debit	5817	5423
Fixed Charges	20,220	15,205
Product Credits, $/D		
(Fuel Gas)	(6869)	(7815)
(LPG)	(5539)	(3439)
Product Upgrade (Octane-bbl/D)	136,417	149,528
Processing Cost, ¢/Oct-bbl	26.0	18.0

(1) See Tabel 7 for Basis.

TABLE 3

TIP/SafeCat vs. Hydrotreater/TIP

Economics (1)

Case	TIP/SafeCat	HDT/TIP
Erected Cost, MM$	13.9	16.4
Operating Cost, $/D		
Utilities	5732	9435
Chemical/Consumption	4772	6778
Catalyst	681	630
Yield Loss	5153	6181
RVP Debit	4355	4274
Fixed Charges	16,525	18,423
Product Credits, $/D		
(Fuel Gas)	(2474)	(3461)
(LPG)	(3744)	(3631)
Product Upgrade (Octane-bbl/D)	152,712	147,445
Processing Cost, ¢/Oct-bbl	20.3	26.2

(1) See Table 7 for Basis.

TABLE 4

Gasoline Pool Description

87 (R+M)/2 -- No LSR Isomerization

Component	BPSD	LV-%
Butanes	1930	4.00
LSR	7100	14.71
FCC Gaso.	17,856	36.98
Poly Gaso.	1354	2.80
Alkylate	4234	8.77
Reformate	15,808	32.74
MTBE	0	0
Total	48,282	100

Gasoline pool (R+M)/2 = 86.95

Reformer Operation

300 psig
96.5 Ron-Clear

TABLE 5

89 (R+M)/2 -- MTBE Addition

Case	Base	MTBE Added
Component (BPSD)		
Butanes	1930	1930
FCC Gasoline	17,856	17,856
Poly Gasoline	1354	1354
Alkylate	4234	4234
LSR Naphtha	7100	7100
Reformate	15,808	15,808
MTBE	--	4598
Total Pool (BPSD)	48,282	52,880
Pool (R+M)/2 (Clear-BPSD)	87	89
Reformer Severity (RONC)	96.5	96.5

TABLE 6

Gasoline Pool Description

89 (R+M)/2 -- No LSR Isomerization

Component	BPSD	LV-%
Butanes	1775	3.57
LSR	7100	14.30
FCC Gaso.	17,856	35.95
Poly Gaso.	1354	2.73
Alkylate	4234	8.52
Reformate	14,847	29.89
MTBE	2500	5.03
Total	49,666	100

Gasoline pool (R+M)/2 = 88.98

Reformer Operation

300 psig
100 Ron-Clear

TABLE 7

Cost Calculations Basis

Product/Feed Values

Component	Value	
LSR	17	\$/bbl
87 (R+M)/2 Clear Gasoline	22.50	\$/bbl
89 (R+M)/2 Clear Gasoline	24.10	\$/bbl
LPG	13	\$/bbl
Fuel Gas	3	\$/MM Btu

Calculations

Isom. Yield Loss = $\triangle$ C_5+ (Feed-Product) Times Feed Value.

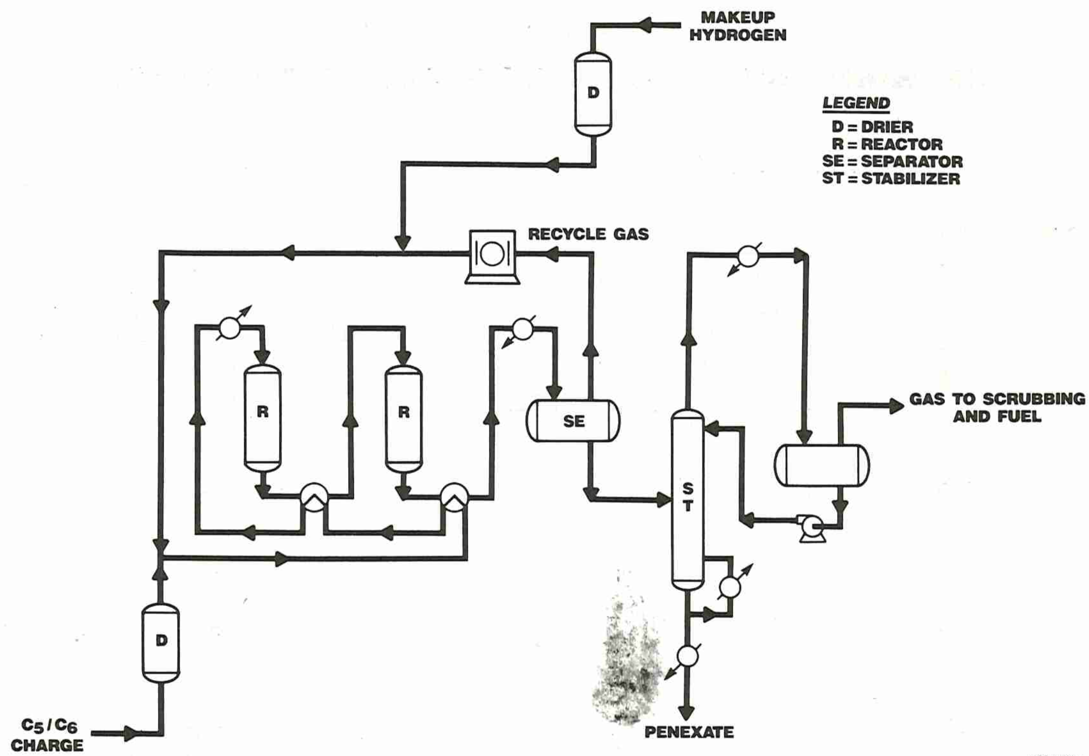
RVP Debit = Value of Butanes Removed from Isomerate to Reduce RVP to Equal Feed.

Fixed Charges = 28% of Total Project Cost Plus Estimated Labor.

Unit Basis:

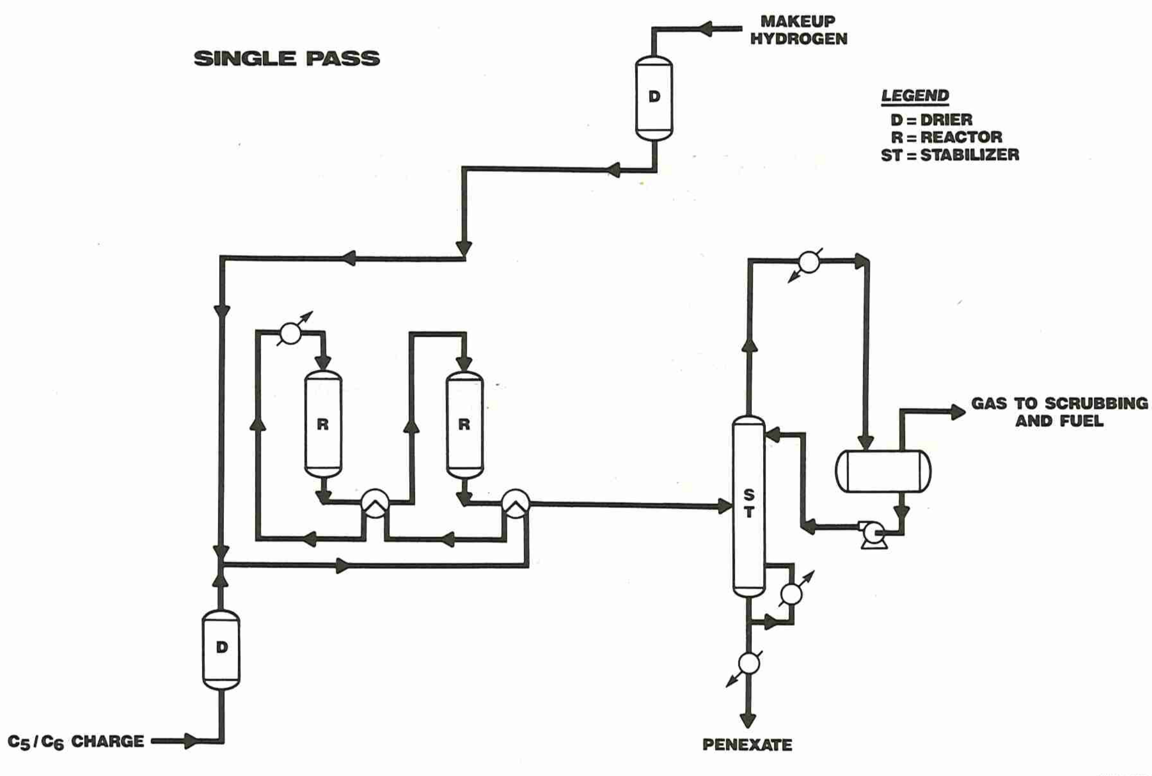
10,000 BPSD, Light Arabian Crude
UOP Modular Construction
U.S. Gulf Coast, 1st Qtr. 1989

FIGURE 1
UOP PENEX PROCESS
SINGLE PASS



UOP 1566-1
UOP 1661B-6

FIGURE 2
UOP PENEX PROCESS
ONCE-THROUGH HYDROGEN



UOP 1566-2
UOP 1661B-7

FIGURE 3

TIP SIMPLIFIED PROCESS FLOW DIAGRAM

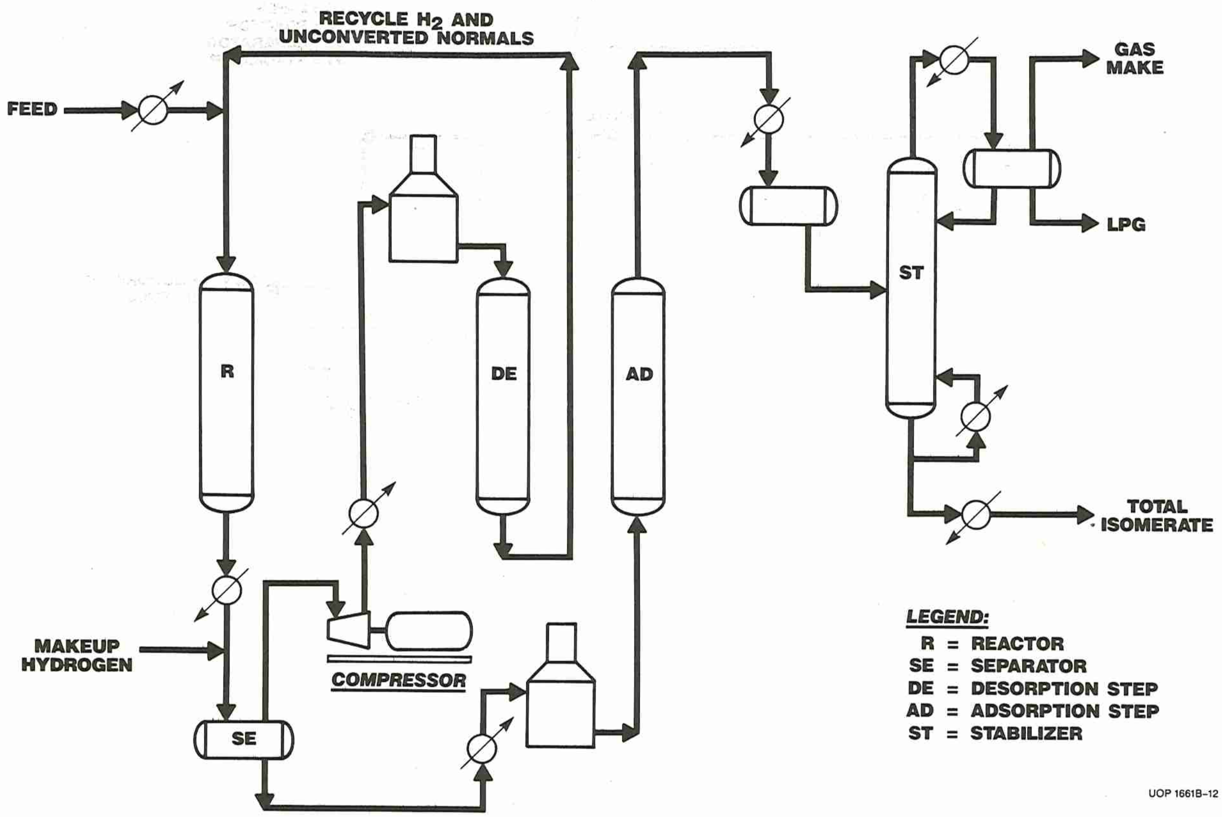


FIGURE 4

INTEGRATED TIP/SafeCat POLYBED PSA