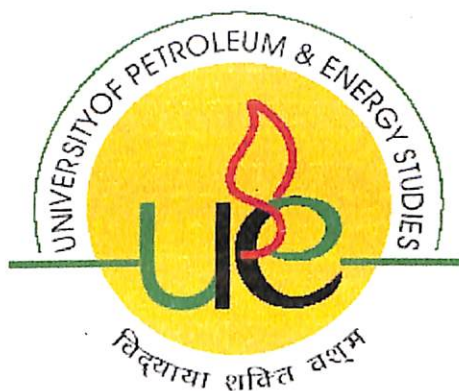A
PROJECT REPORT ON

"MATERIAL BALANCE FOR THE OPTIMIZATION OF FUEL REFORMERS"

BY
Rudresh Nautiyal
B.tech APE-Downstream

UNDER THE SUPERVISION
OF
Dr. R.P. Badoni
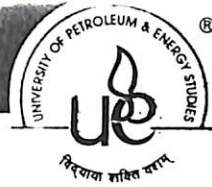
College of Engineering
University of Petroleum & Energy Studies, Dehradun
May, 2009

CERTIFICATE

This is to certify that Rudresh Nautiyal, has completed the Major Project.

The project work entitled "Optimization Of fuel Reformers" embodies the studies done by him under my supervision.

R.P. Bewani
May 14, 2009

Dr. R.P. Badoni

Distinguished Professor

UPES

'porate Office:
lrocarbons Education & Research Society
Floor, PHD House,
Siri Institutional Area
lust Kranti Marg, New Delhi - 110 016 India
+91-11-41730151-53 Fax +91-11-41730154

Main Campus:
Energy Acres,
PO Bidholi Via Prem Nagar,
Dehradun - 248 007 (Uttarakhand), India
Ph.: +91-135-2102690-91, 2694201/ 203/ 208
Fax: +91-135-2694204

Regional Centre (NCR) :
SCO. 9-12. Sector-14.
Gurgaon 122 007
(Haryana). India.
Ph: +91-124-4540 300
Fax: +91-124-4540 330

Regional Centre (Rajahmundry):
GIET. NH 5, Velugubanda,
Rajahmundry - 533 294,
East Godavari Dist., (Andhra Pradesh), India
Tel: +91-883-2484811/ 855
Fax: +91-883-2484822

ACKNOWLEDGEMENT

CONTENTS:

ABSTRACT

Catalytic reforming is one of the major processes used in secondary refining operations. This is mainly used for increasing the octane number of fuel and improving fuel quality through operations involving low severity. Today, this process is a requirement in every petroleum refinery as higher quality gasoline is required to meet the stringent emission norms and for higher efficiency engines. Alternately, it can also be used to produce aromatics mainly BTX which are the building blocks in the petrochemical industry, through higher severity operations. This is the only process that produces hydrogen as a byproduct which is an expensive as well as a feed to many of the units in a refinery.

Catalytic reforming is a chemical process involving conversion by rearranging low octane refinery naphtha's which are napthenes and straight chain paraffin's into high octane gasoline products that are complex molecules known as reformate. In so doing, the process separates hydrogen atoms from the hydrocarbon molecules and produces very significant amounts of byproduct hydrogen gas for use. In Continuous Catalytic Reforming, the catalyst(Pt/Re on an alumina base) is continuously regenerated by burning of coke thereby resolving the problem of degradation of the catalyst and enhancing the overall efficiency of the process.

Through the project I am able to study the various catalytic reforming processes and the emerging technologies in the field. In the later part of this project I focused on UOP's Continuous Catalytic Reforming process and were able to understand the process chemistry, major reactions, catalysts, and the process variables involved. I have dealt with the optimization of the process by doing material balance, hydrogen balance, and cyclic ring balance calculation of the reformer..

INTRODUCTION TO CATALYTIC REFORMING

1.1. *Catalytic Reforming:*

Catalytic reforming is a chemical process used to convert petroleum refinery naphtha's, typically having low octane ratings, into high-octane liquid products called **reformates** which are components of high-octane gasoline (also known as petrol). Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstock's as well as breaking some of the molecules into smaller molecules. The overall effect is that the product reformate contains hydrocarbons with more complex molecular shapes having higher octane values than the hydrocarbons in the naphtha feedstock. In so doing, the process separates hydrogen atoms from the hydrocarbon molecules and produces very significant amounts of byproduct hydrogen gas for use in a number of the other processes involved in a modern petroleum refinery. Other byproducts are small amounts of methane, ethane, propane and butanes.

This process is quite different from and not to be confused with the catalytic steam reforming process used industrially to produce various products such as hydrogen, ammonia and methanol from natural gas, naphtha or other petroleum-derived feedstock's. Nor is this process to be confused with various other catalytic reforming processes that use methanol or biomass-derived feedstock's to produce hydrogen for fuel cells or other uses.

1.2 History

Universal Oil Products (also known as UOP) is a multi-national company developing and delivering technology to the petroleum refining, natural gas processing, petrochemical production and other manufacturing industries. In the 1940s, an eminent research chemist named Vladimir Haensel working for UOP developed a catalytic reforming process using a catalyst containing platinum. Haensel's process was subsequently commercialized by UOP in 1949 for producing a high octane gasoline from low octane naphtha's and the UOP process become known as the Platforming process. The first Platforming

unit was built in 1949 at the refinery of the Old Dutch Refining Company in Muskegon, Michigan.

In the years since then, many other versions of the process have been developed by some of the major oil companies and other organizations. Today, the large majority of gasoline produced worldwide is derived from the catalytic reforming process.

To name a few of the other catalytic reforming versions that were developed, all of which utilized a platinum and/or a rhenium catalyst:

- Rheniforming: Developed by Chevron Oil Company.
- Powerforming: Developed by Esso Oil Company, now known as ExxonMobil.
- Magnaforming: Developed by Englehard Catalyst Company and Atlantic Richfield Oil Company.
- Ultraforming: Developed by Standard Oil of Indiana, now a part of the British Petroleum Company.
- Houdriforming: Developed by the Houdry Process Corporation.
- CCR Platforming: A Platforming version, designed for continuous catalyst regeneration, developed by UOP.
- Octanizing: A catalytic reforming version developed by Axens, a subsidiary of Institut francais du petrole (IFP), designed for continuous catalyst regeneration.

During this project we shall be dealing with UOP's CCR Platforming process.

UOP PLATFORMING PROCESS

2.1. PROCESS EVOLUTION

The Platforming process is a UOP developed and engineered catalytic reforming process in widespread use today throughout the petroleum and petrochemical industries. The first UOP Platforming unit went on-stream in 1949. The Platforming process has since become a standard feature in refineries worldwide.

In the Platforming process, light petroleum distillate (naphtha) is contacted with a platinum- containing catalyst at elevated temperatures and hydrogen pressures ranging from 345 to 3450 kPa (50 to 500 lb/in2 gage). Platforming produces a high-octane liquid product that is rich in aromatic compounds. Chemical-grade hydrogen, light gas, and liquefied petroleum gas (LPG) are also produced as reaction byproducts.

Originally developed to upgrade low-octane-number straight-run naphtha to high octane motor fuels, the process has since been applied to the production of LPG and high purity aromatics.' A wide range of specially prepared platinum based catalysts permit tailored processing schemes for optimum operation. With proper feed preparation, Platforming efficiently handles almost any refinery naphtha.

Since the first Platforming unit was commercialized, UOP has been at the industry forefront in advancing reforming technology. UOP has made innovations and advances in process-variable optimization, catalyst formulation, equipment design, and maximization of liquid and hydrogen yields. Since higher yields and octane are obtained at low pressure and high severity, innovations at UOP were driven to meet these objectives while controlling the coke deposition and catalyst deactivation.

The first Platforming units were designed as semiregenerative (SR), or fixed-bed, units employing monometallic catalysts. Semiregenerative Platforming

units are periodically shut down to regenerate the catalyst. This regeneration includes burning off catalyst coke and reconditioning the catalyst's active metals. To maximize the length of time (cycle) between regenerations, these early units were operated at high pressures in the range of 2760 to 3450 kPa (400 to 500 lb/in2 gage).

Legend

H = Heater
R = Reactors
S = Separator
ST = Stabilizer
RE = Receiver
FE = Feed-Effluent Exchanger

UOP Platforming process.
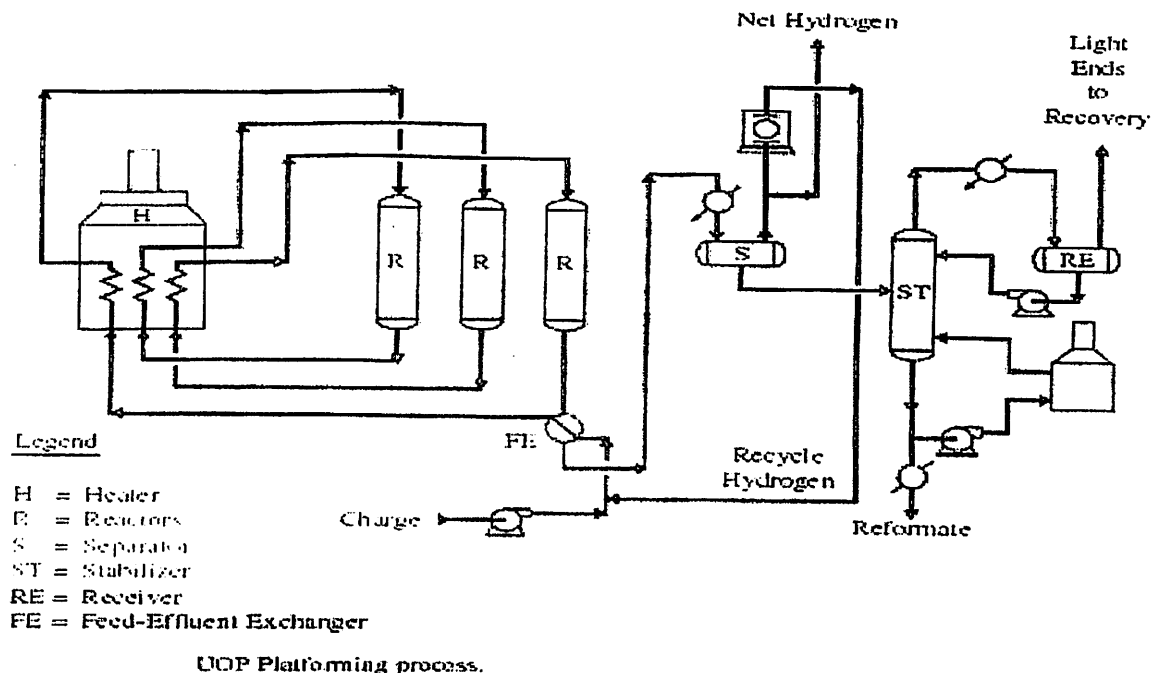
Figure 1

A typical SR Platforming flow diagram is presented in Fig. 1. In the process flow, feed to the Platforming unit is mixed with recycled hydrogen gas, preheated by a feed- effluent exchanger, further heated to reaction temperature by a fired heater, and then charged to the reactor section. Because most of the reactions that occur in the Platforming process are endothermic, the reactor section is separated into several stages, or reactors. Fired heaters are installed between these reactors to reheat the process stream up to the correct temperature for the next stage. Effluent from the last reactor is cooled by exchanging heat with the feed for maximum heat recovery. Additional cooling to near-ambient temperature is provided by air or

water cooling. The effluent is then charged to the separation section, where the liquid and gas products are separated. A portion of the gas from the separator is compressed and recycled to the reactor section. The net hydrogen produced is sent to hydrogen users in the refinery complex or to the fuel header. The separator liquid is pumped to a product stabilizer, where the more-volatile light hydrocarbons are fractionated from the high-octane liquid product.

UOP initially improved the Platforming process by introducing bimetallic catalysts to SR Platforming units. These catalysts enabled a lower-pressure, higher-severity operation: about 1380 to 2070 kPa (200 to 300 lb/in2 gage), at 95 to 98 octane with typical cycle lengths of 1 year. The increased coking of the catalyst at the higher severity limited the operating run length and the ability to further reduce pressure. Catalyst development alone could not solve these problems; process innovations were needed. In the 1960s, cyclic reforming was developed to sidestep this barrier. Cyclic reforming employs fixed-bed reforming, but the reactors can be individually taken off-line, regenerated, and then put back into service without shutting down the unit and losing production.

UOP recognized the limitations of fixed-bed catalyst stability and so commercialized Platforming with continuous regeneration, the CCR* Platforming process, in 1971.
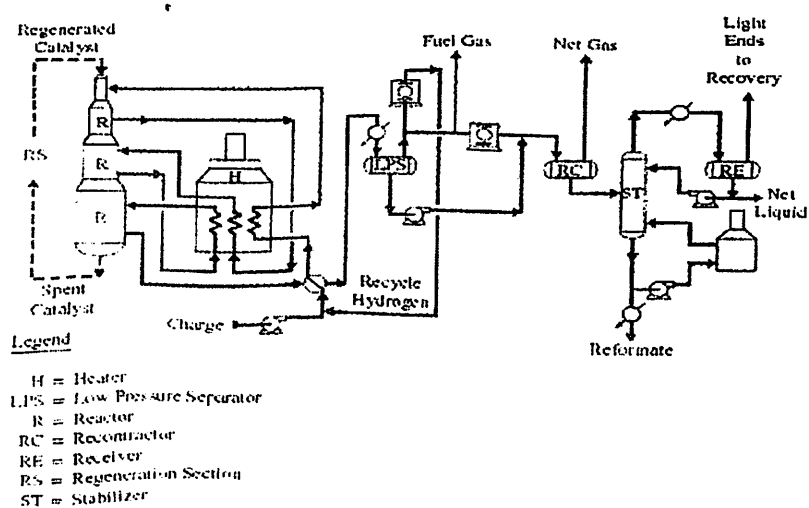

Legend

H = Heater
LPS = Low Pressure Separator
R = Reactor
RC = Recontactor
RE = Receiver
RS = Regeneration Section
ST = Stabilizer

UOP CCR Platforming process.

Figure 2

The process employs continuous catalyst regeneration in which catalyst is continuously removed from the last reactor, regenerated in a controlled environment, and then transferred back to the first reactor (Fig. 2). The CCR Platforming process represents a step change in reforming technology. With continuous regeneration, coke laydown is no longer an issue because the coke is continuously burned off and the catalyst is reconditioned to its original performance. The CCR Platforming process has enabled ultralow-pressure operations at 345 kPa (50 lb/in2 gage) and produced product octane levels as high as 108. The continuous regeneration approach has been very successful with more than 95 percent of the new catalytic reformers being designed as CCR Platforming units. In addition, many units that were originally built as SR Platforming units have been revamped to CCR Platforming units.

In summary, the UOP Platforming process has evolved continuously throughout its history. The operating pressure has been lowered by more than 2760 kPa (400 lb/in2 gage), and hydrogen yield has doubled. Product octane was increased by more than 12 numbers along with a C5+ yield increase of 2 liquid volume percent (LV %). The evolution of UOP Platforming performance is depicted in Fig. 3, which shows the increase in both C5+ yield and octane through time and innovation compared to the theoretical limit.
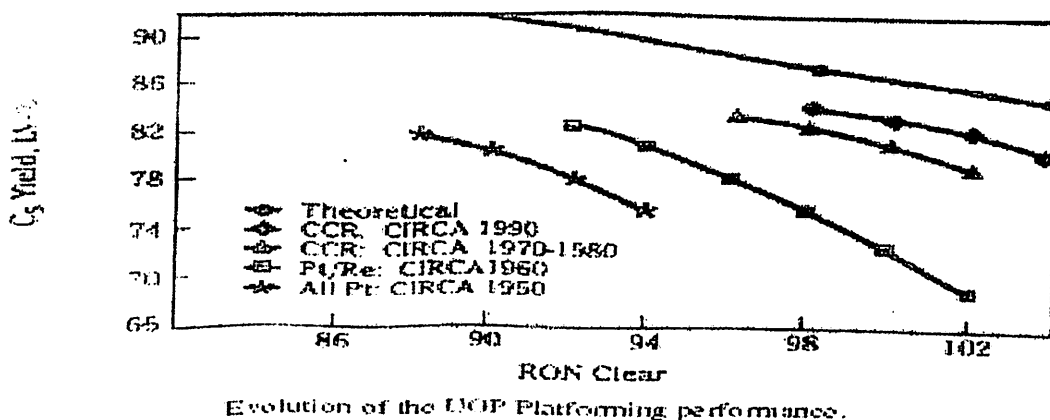

Evolution of the UOP Platforming performance.

Figure 3

EMERGING TECHNOLOGIES

3.1. RZ PLATFORMING

RZ Platforming is the latest development in UOP's long tradition of reforming process improvements. The process is built around a new type of catalyst called RZ¬100. RZ-100 is a zeolitic catalyst, activated with platinum, that gives the highest obtainable yields of benzene (8) and toluene (T) from naphtha feedstocks. The RZ process is ideally suited for use in aromatics production facilities especially when large amounts of benzene are required. The ability of the RZ Platforming process to convert light, paraffinic feeds and its flexibility in processing straight-run naphtha fractions provide many options for improving aromatics production and supplying highly desired hydrogen.

3.2. Chemistry and Catalyst

The function of the 8T reformer is to efficiently convert paraffins and naphthenes to aromatics with as little naphthene ring opening or paraffin cracking as possible. The cracking reactions lead to the production of undesirable light gas products at the expense of 8T yields and hydrogen.

The RZ-100 catalyst differs greatly in the production of aromatics from conventional reforming catalyst. The selectivities of RZ Platforming for toluene and benzene are approximately factors of 2 and 4 greater, respectively, than previous state-of-the-art reforming catalysts. Figure. 4 illustrates the differences for aromatic yields as a function of the feed paraffin carbon number.
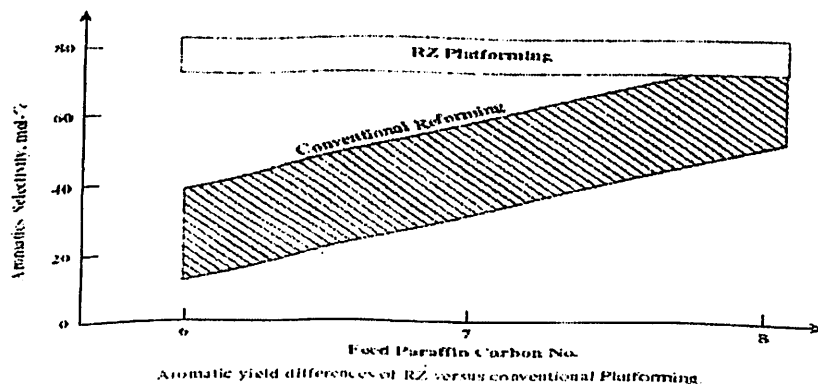

Figure 4

The RZ-100 catalyst selectivity to BT is achieved through platinum-catalyzed cyclization of paraffins in contrast to the predominantly acid-catalyzed route in conventional reforming. The absence of acid sites allows the RZ-100 catalyst to form aromatics without producing significant light by-products through cracking. Though significantly different in reaction mechanism and aromatic selectively, the RZ- 100 catalyst is operated in a. similar fashion to conventional fixed-bed reforming catalysts. The extruded catalyst is operated with cycle lengths of 6 months to 1 year. During the cycle, the temperature is increased to maintain BT production as the catalyst is deactivating. Cycle lengths are determined when temperature limits are reached or when a shutdown of other operating units in the refinery provides a convenient opportunity for RZ-100 catalyst regeneration. Once it is regenerated, the catalyst performance is identical to that of the previous cycle.

Process Description

The RZ Platforming process is similar in configuration to other Platforming processes; however, the greater conversion of C6 and C7 hydrocarbons translates to higher heats of reaction. If maximum yields of Band T are desired, a five-reactor system is usually employed. A simplified flow schematic is shown in Fig. 5. Treated naphtha feed is combined with recycled hydrogen gas and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and sent to the reactor section. Adiabatic, radial-flow reactors are arranged in a conventional side-by-side pattern. The predominant reactions are endothermic so an interheater is used between each reactor to reheat the charge to the reaction temperature. Flue gas from the fired heaters is typically used to generate high-pressure steam, but other heat integration options are available.

The effluent from the last reactor is heat-exchanged against the combined feed, cooled, and phase-split into vapor and liquid products in a separator. The vapor phase is rich in hydrogen gas, and a portion of the gas is compressed and recycled to the reactors. The net hydrogen-rich gas is

compressed and charged together with the separator liquid phase to the product recovery section. The liquid product from the recovery section is sent to a stabilizer where light saturates are removed from the C6+ aromatic product. Since zeolite reforming catalysts are more sensitive to sulfur poisoning than conventional Platforming catalyst, a sulfur scavenger system is used to maintain the sulfur concentration below 0.1 ppm.

The RZ-100 catalyst deactivates over time at reaction conditions and needs to be regenerated. The typical cycle lengths are 8 to 12 months. The catalyst system is designed to be regenerated ex situ.

3.4. *Process Performance*

Although CCR Platforming is the most efficient process for producing xylenes (X) from heavier naphtha fractions, the conversion of C6 and C7 paraffins to aromatics is normally below 50 percent, even at low pressure. The RZ-100 catalyst offers high aromatic selectivity even when processing the most difficult C6 and C7 paraffin feed components.

The selectivity and yield advantages of the RZ -100 catalyst can be demonstrated by examining pilot-plant data using a raffinate feed consisting primarily of C6 and C7 paraffins. The pilot-plant feed LHSV and pressure were held constant while the reactor temperature was varied to obtain a wide range of paraffin conversion. Figure 6 shows that the RZ-100 catalyst produced up to 25 wt % more aromatics at a given paraffin conversion. Since more of the light paraffins were selectively converted to aromatics, less hydrogen was consumed for other reactions such as cracking. For the pilot-plant tests, the hydrogen yield for the RZ-100 catalyst was about double that of the CCR Platforming catalyst.

Aromatic yields from raffinate.
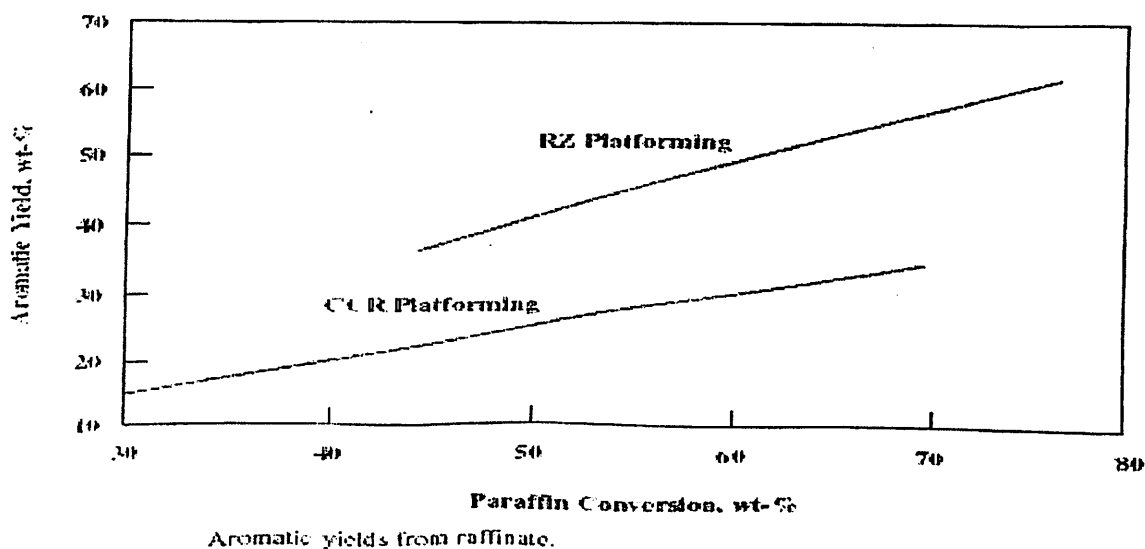
Figure 5

3.5. *Feedstock*

Feedstocks to the RZ Platforming unit can range from extraction unit raffinate to BTX naphtha. A very effective application for the RZ-100 catalyst is the production of aromatics and hydrogen from light, paraffin feeds, such as a BT raffinate. The RZ¬100 catalyst can also be used in parallel with a second reforming unit (semi regenerative or CCR unit) to optimize the production of the desired aromatics by processing different fractions of the hydrotreated feed. In such cases, the conventional reformer can be dedicated to processing the heavier feed fraction, taking advantage of its superior ability to produce xylenes. The light naphtha, which is rich in C6 and C7 components, can be routed to the RZ Platforming unit, where selectivity for converting light paraffins to benzene and toluene is greatest.

3.6. Sample Case Study : Yield Comparison between CCR Platforming and RZ Platforming

TABLE 1

	Overall Yield Comparison, wt %	
	Conventional CCR platformer	Split-flow RZ Platformer
Hydrogen	2.91	4.46
Gas	12.23	14.31
LPG	8.68	5.80
Raffinate	15.24	0.00
Benzene	15.93	29.38
Para-Xylene	38.82	39.93
Heavies	6.07	6.13
Naphtha	100.00	100.00
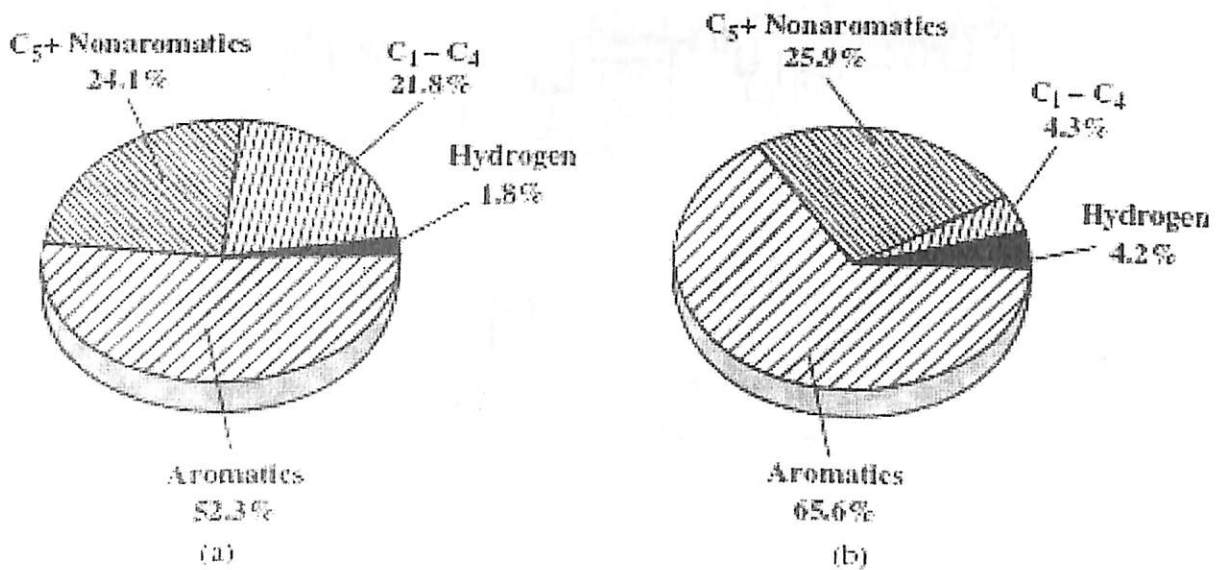
Yield differences for light naphtha feed. (a) Conventional semiregenerative; (b) RZ Platforming.

Here we have a PFD of a conventional CCR and split flow containing a RZ and a CCR.

(a)

(b)
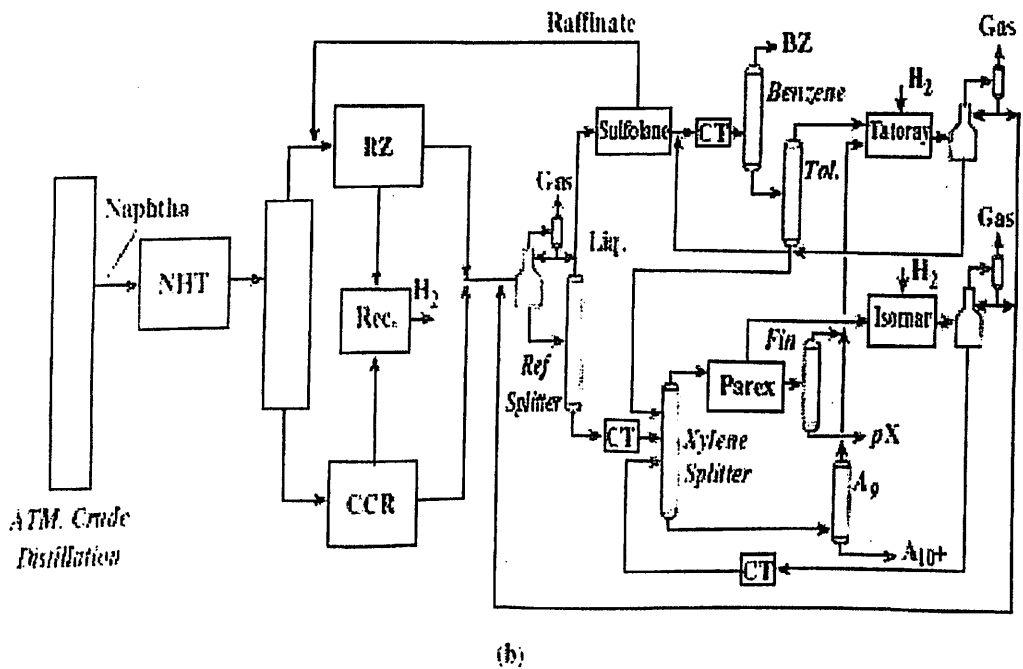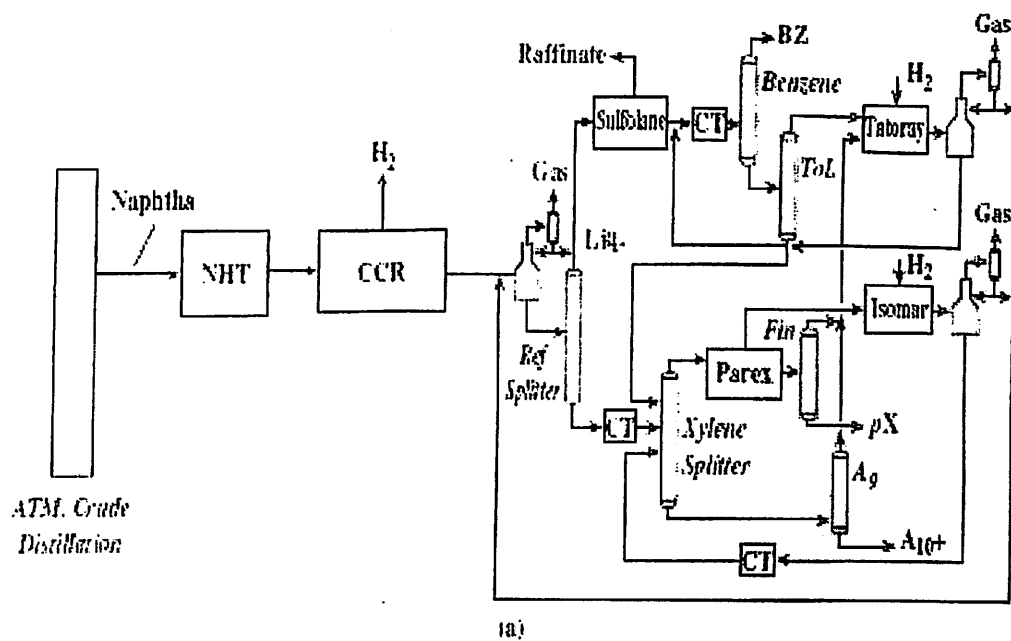
Use of CCR and RZ Platforming units. (a) CCR case; (b) split-flow case.

Figure 7

CONTINUOUS CATALYTIC REFORMING

4.1 *INTRODUCTION*

In the years following the invention of Platforming, the need for high-octane gasoline blend components and the demand for aromatics for petrochemicals steadily increased. This increasing market demand required refiners to operate their Platforming units at everhigher severity. Eventually, improvements in the catalyst " and process could not keep up, and the need to regenerate catalyst at shorter and shorter intervals became a serious limitation of the SR Platforming units. UOP developed the CCR Platforming process to overcome this limitation. In the CCR Platforming unit, partially coked catalyst in the reactors is continuously replaced with catalyst that has been freshly regenerated in an external regenerator (CCR section) to maintain a low average coke for the reactor catalyst. **Thus, continuous highselectivity and high-activity characteristics associated with new catalyst can be achieved at significantly higher severities than with the SR Platformi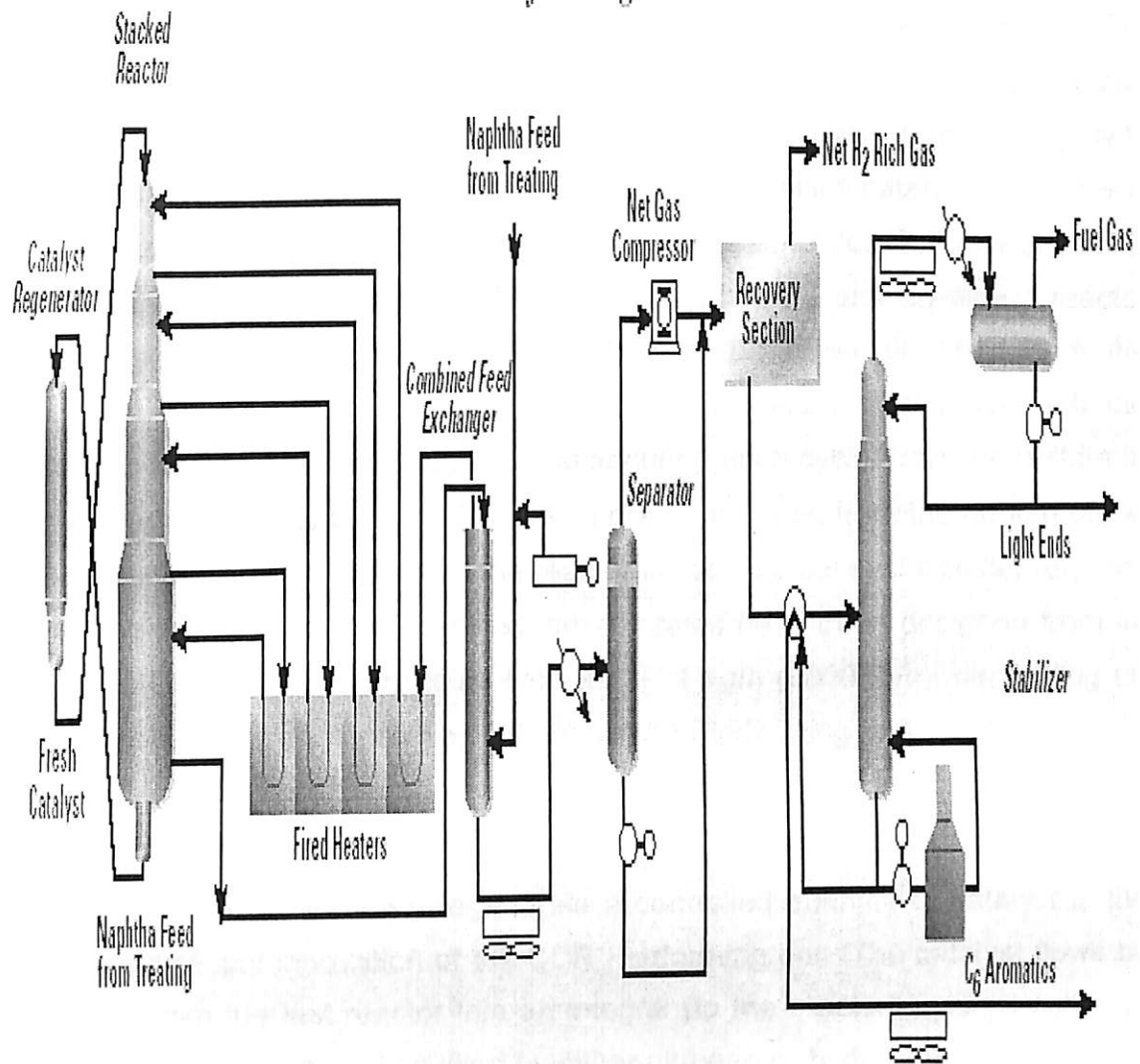ng process.** For example, a SR Platforming unit operates at a severity that steadily builds coke up on the catalyst surface over the length of a cycle (6 to 18 months), at which point the unit is shut down and the catalyst regenerated. Throughout the cycle, yields decline. In contrast, with a modern CCR Platforming unit, the catalyst is regenerated approximately every 3 days, and yield remains constant at fresh catalyst levels.

The CCR Platforming flow scheme incorporates many engineering innovations. Depending on the size of the unit, many SR Platforming units are also built to include some of these innovations. This design allows for an easier transition between SR and CCR Platforming units if the SR Platforming unit is later converted to meet future operating requirements.

CCR Platforming Process

Stacked Reactor

Catalyst Regenerator

Fresh Catalyst

Naphtha Feed from Treating

Fired Heaters

Naphtha Feed from Treating

Combined Feed Exchanger

Net Gas Compressor

Separator

Recovery Section

Net H$_2$ Rich Gas

Fuel Gas

Light Ends

Stabilizer

C$_6$ Aromatics

4.2. Movable-Catalyst-Bed System

In a conventional SR Platforming unit, the reactors are configured side-by-side. The CCR Platforming unit uses a UOP-patented reactor stack. The reactors are stacked one on top of another to achieve a compact unit that minimizes plot area requirements. The catalyst flows gently by gravity downward from reactor to reactor, and this flow simplifies catalyst transfer and minimizes attrition. Catalyst transfer is greatly simplified in comparison to other reforming technologies, which employ side-by-side reactor configurations that require the catalyst to be pneumatically lifted from the bottom of each reactor to the top of the next reactor. In contrast, with the reactor stack, catalyst is lifted only twice during each cycle: from the bottom of the reactor stack to the top of the regenerator and then from the bottom of the regenerator back to the top of the reactor stack. The catalyst transfer requires no operator intervention. Catalyst transfer rates have been designed from as low as 91 kg/h (200 lb/h) to as high as 2721 kg/h (6000 lb/h), depending on the capacity and the operating severity of the Platforming unit.

4.3 CCR System

The ability to continuously regenerate a controlled quantity of catalyst is the most significant innovation of the CCR Platforming unit. The catalyst flows by gravity from the last reactor into an integral (to the reactor) catalyst collector vessel. The catalyst is then lifted by either nitrogen or hydrogen lifting gas to a catalyst hopper above the regeneration tower. Catalyst flows to the regeneration tower, where the catalyst is reconditioned. Regenerated catalyst is then returned to the top of the reactor stack by a transfer system similar to that used in the reactor-regenerator transfer. Thus, the reactors are continuously supplied with freshly regenerated catalyst, and product yields are maintained at fresh catalyst levels. The regeneration and reactor sections of the unit are easily isolated to permit a shutdown of the regeneration system for normal inspection or maintenance without interrupting the Platforming operation.

Improvements are continuously being made in the CCR regeneration section design. In addition to its atmospheric and pressurized regenerators, UOP

introduced the CycleMax* regenerator in 1995 which combines new innovations with the best . aspects of previous CCR designs at lower cost.

4.4. Low-Pressure-Drop Features

Minimum pressure drop in the reactor section is critical for efficient ultralow-pressure operation. Low pressure drop minimizes recycle gas compressor differential pressure and horsepower. The result is lower utility consumption. The cost for even 1 lb of additional pressure drop across the compressor is high. Minimum pressure drop also permits the operation at the lowest possible average reactor pressure, which increases reformate and hydrogen yields. UOP employs a variety of special equipment to minimize the pressure drop throughout the plant circuit. Either vertical combined feed-effluent exchangers (VCFEs) or new PACKINOX welded-plate exchangers introduced in the 1990s are used to maximize thermal efficiency and minimize pressure drop. The patented reactor stack design, fired heater design, and plot-plan layout further reduce plant pressure drop to achieve minimum compression costs.

4.5. Secondary-Recovery Schemes

Several innovative schemes for increased liquid recovery and separator gas purification have been developed. The need for increasing liquid recovery is more critical with the lower- pressure designs, where the production of hydrogen and C5+ material is increased as a result of more-selective processing. This advantage can be lost if a recovery system is not installed downstream of the reactor section. At low operating pressures, the flash pressure of the separator has been reduced. Consequently, the vapor liquid equilibrium thermodynamically allows for more C4's, C5's, and C6+ material to leave with the vapor, resulting in valuable C5+ product loss and lower-purity hydrogen production. To avoid this loss, several types of improved recontacting schemes have been developed.

One scheme often used is reactor-effluent vapor-liquid recontacting. In this scheme, reactor effluent, after being cooled, is physically separated into vapor and liquid portions. Part of the vapor is directed to the recycle-compressor suction for use as recycle gas. The remaining vapor, called the net separator

gas, is compressed by a booster compressor and discharged into either a drum or an adsorber. The liquid from the separator is also pumped to the drum or absorber to recontact with the net separator gas at elevated pressure to obtain increased liquid recovery and hydrogen purity.

Another method involves chilling the net separator gas. Depending on downstream pressure requirements, net gas from either the compressor suction or discharge is cooled to approximately 5°C (41°F) by a refrigeration system. Separation of the vapor and liquid at a low temperature improves hydrogen purity and recovers additional liquid, which would be routed to the stabilizer with the liquid from the low¬pressure separator. In addition, proprietary systems have been developed that even more efficiently recover the liquid product. UOP offers one such system, RECOVERY PLUS, * that improves the recovery of the liquid product at minimum operating cost.

4.6. Advantages of CCR Platforming

From both economic and technical standpoints, the CCR Platforming process has significant advantages over the SR Platforming process. The advantages are discussed below:

- The CCR Platforming unit has the highest possible yields because it is capable of the lowest possible pressure operation. If operated at the same conditions, the SR Platforming catalyst is completely deactivated after only a few days of operation. In contrast, the high catalyst coking rate is easily managed in CCR Platforming by continuously regenerating the catalyst. Both the hydrogen and the Cs + yields are maximized with the CCR Platforming process. The Cs + yield advantage is illustrated in Fig. 8, and the hydrogen yield advantage is shown in Fig. 9.
- Equally important to high yields in the economics' of reforming are constant non declining yields. Yields decline steadily from the beginning to the end of a cycle in SR Platforming as the catalyst is deactivated by coke deposition. With the CCR Platforming process, the

reformate, aromatics and hydrogen yields remain constant. This result is particularly important for downstream users because inconsistent quality can lead to their products not meeting specifications. The constancy of the yields is achieved by the CCR section, which ensures proper redispersion of the metals and chloride balance to maintain fresh catalyst activity.

- CCR Platforming units have higher on-stream efficiency and are able to handle upset scenarios without long-term shutdown or significant decline in performance. For example, a compressor-trip or feed-upset scenario can lead to significant problems with the SR Platforming unit because of increased coke levels, which inevitably shorten catalyst cycle length. However, the continuous regeneration of catalyst in the CCR Platforming unit allows for faster resumption of normal operations. The independent operation of the reactor and catalyst regeneration sections and the robust design of the CCR Platforming unit enable the greater on¬stream availability for the CCR Platforming unit. Customer surveys indicate that the average time between planned turnarounds is 3.4 years .

- Since the catalyst is not regenerated in situ, the reactor section operates only in its primary function of providing the catalytic environment for the reforming reactions. It is therefore not exposed to harsh regeneration conditions and is less prone to corrosion and fouling than SR Platforming.
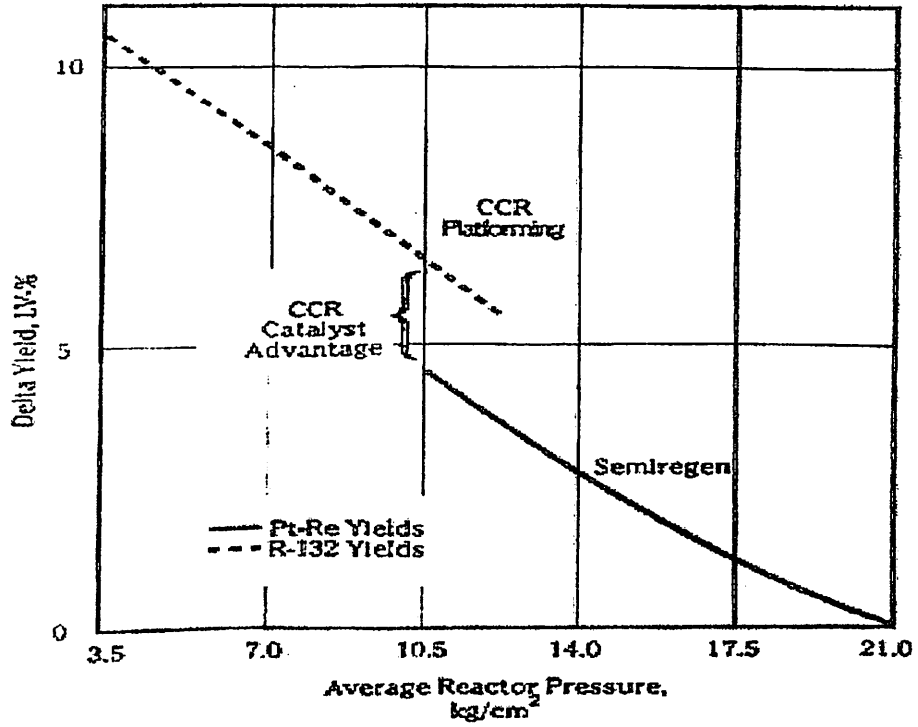
The C₅+ yield at decreasing pressure.

Figure 8
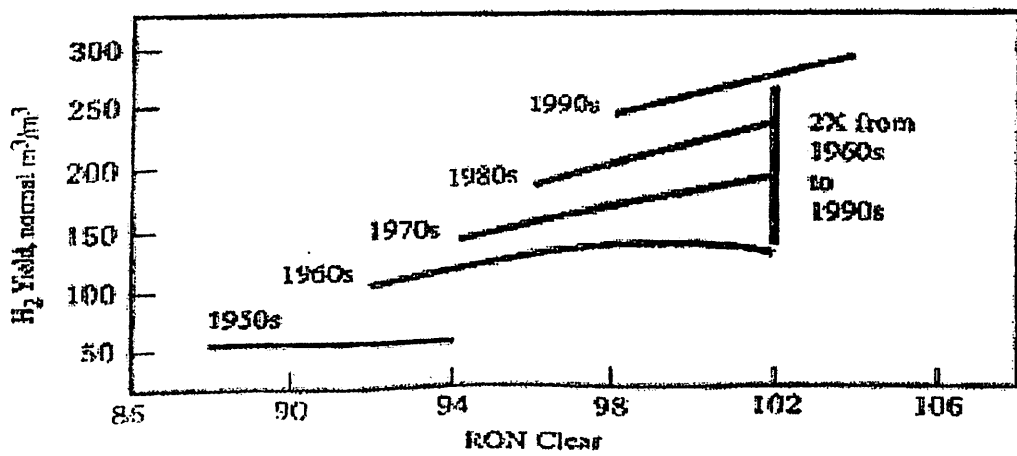
Note: 1950s — All Pt
      1960s = Pt/Re
      1970s = CCR
      1990s = Low-Pressure CCR

Yield efficiency improvement.

Figure 9

UOPCOMMERCIAL EXPERIENCE

5.1 INTRODUCTION

UOP has designed more than 730 Platforming (both SR and CCR) units around the world with a total feedstock capacity of more than 9.1 million barrels per stream-day (BPSD).

The feedstocks range from benzene-toluene (BT) cuts to full-range, lean Middle East naphthas and rich U.S. and African naphthas and hydrocracked stocks with capacities ranging from 150 to 60,000 BPSD. Research octane numbers run from 93 to 108 over a wide range of catalysts.

5.2. CURRENT SCENARIO

The UOP CCR Platforming process is the most successful reforming process offered by any licenser. As of mid-2002, UOP's unparalleled commercial experience includes

- 171 UOP CCR Platforming units operating around the world

- 52 units operating at state-of-the-art reactor pressure of 75 lb/in2 gage

- 82 units operating at or below 100 lb/in2 gage reactor pressure

- 4,000,000 BPSD CCR Platforming unit operating capacity

- 99.5% of all CCR Platforming units ever started up still operating

- 31 more UOP CCR Platforming units in design and construction

PROCESS CHEMISTRY

6.1. Feed and Product Compositions

The Platforming naphtha charge typically contains C6 through C 11 paraffins, naphthenes, and aromatics. The primary purpose of the Platforming process is to produce aromatics from the paraffins and naphthenes. The product stream is a premium-quality gasoline blending component because of the high-octane values of the aromatics. Alternatively, the aromatics-rich product stream can be fed to a petrochemical complex where valuable aromatic products such as benzene, toluene, and xylene (BTX) can be recovered. In motor fuel applications, the feedstock generally contains the full range of C6 through C11 components to maximize gasoline production from the associated crude run. In petrochemical applications, the feedstock may be adjusted to contain a more-select range of hydrocarbons (C6 to C7, C6 to C8, C7 to C8, and so forth) to tailor the composition of the reformate product to the desired aromatics components. For either naphtha application, the basic Platforming reactions are the same.

Naphthas from different crude sources vary greatly in their hydrocarbon composition and thus in their ease of reforming. The ease with which a particular naphtha feed is processed in a Platforming unit is determined by the mix of paraffins, naphthenes, and aromatics in the feedstock. Aromatic hydrocarbons pass through the unit essentially unchanged. Naphthenes react relatively easily and are highly selective to aromatic compounds. Paraffin compounds are the most difficult to convert, and the relative severity of the Platforming operation is determined by the level of paraffin conversion required. Lowseverity (low-octane) operations require little paraffin conversion, but higher-severity operations require a significant degree of conversion.

Naphthas are characterized as lean (low naphthene and aromatic content) or rich (high naphthene and aromatic content). Rich naphthas, with a higher proportion of naphthene components, are easier to process in the Platforming

unit. Fig. 10 demonstrates the effect of naphtha composition on the relative conversion of the feedstock under constant operating conditions in the Platforming process. A rich naphthenic charge produces a greater volumetric yield of reformate than does a lean
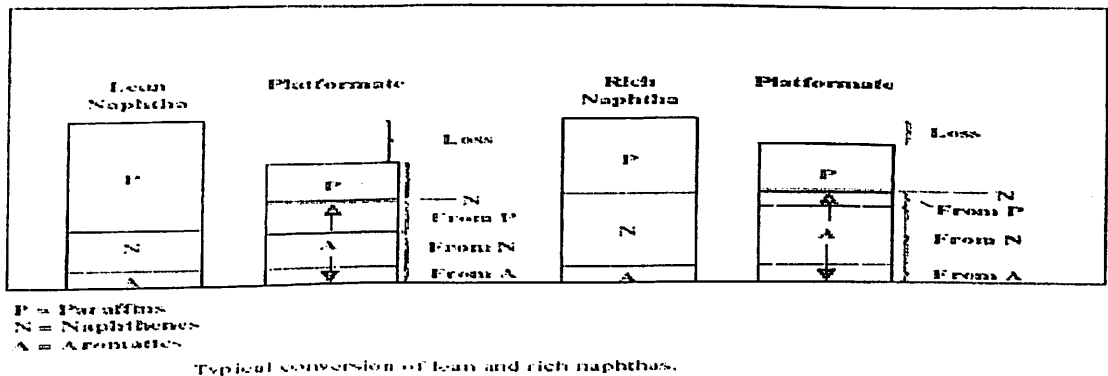
Figure 10

6.2. Reactions

Platforming reactions can generally be grouped into four categories: dehydrogenation, isomerization, dehydrocyclization, and cracking. The reactions are promoted by two kinds of active sites on the catalyst, acidic and metallic. The extent to which each of the reactions occurs for a given Platforming operation depends on the feedstock quality, operating conditions, and catalyst type.

Because the Platforming feed is made up of many paraffin and naphthene isomers, multiple reforming reactions take place simultaneously in the Platforming reactor. The rates of reaction vary considerably with the carbon number of the reactant. Therefore, these multiple reactions occur in series and in parallel to one another. The generalized reaction network is illustrated in Fig.11.

Figure 11

MAJOR REACTIONS

7.1. Dehydrogenation of Naphthenes:

The principal Platforming reaction in producing an aromatic from a naphthene is the dehydrogenation of an alkylcyclohexane. This reaction takes place rapidly and proceeds essentially to completion. The reaction is highly endothermic, is favored by high reaction temperature and low pressure, and is promoted by the metal function of the catalyst. Because this reaction proceeds rapidly and produces hydrogen as well as aromatics, naphthenes are the most desirable component in the Platforming feedstock.
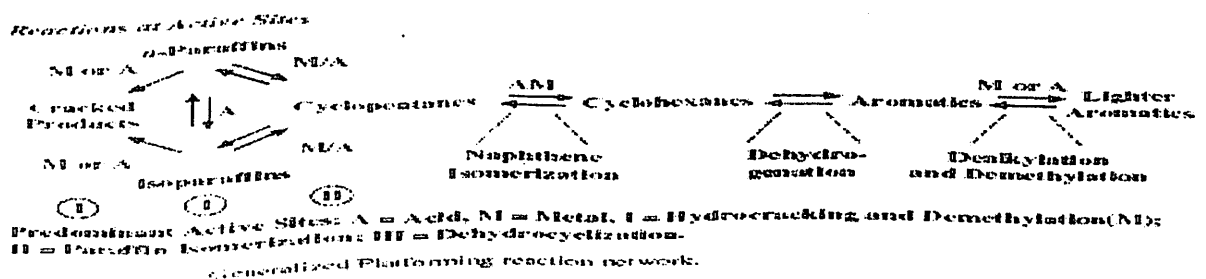
Dehydrogenation of Naphthene

$$\text{cyclohexane-R} \rightleftharpoons \text{benzene-R} + 3H_2$$
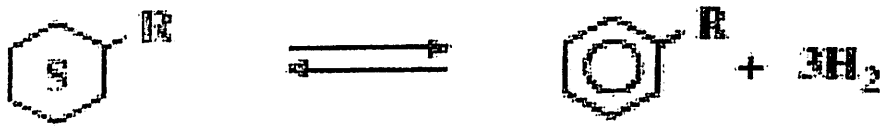
7.2. Isomerization of Paraffins and Naphthenes:

The isomerization of an alkylcyclopentane to an alkylcyclohexane must take place before an alkylcyclopentane can be converted to an aromatic. The reaction involves ring rearrangement, and thus ring opening to form a paraffin is possible. The paraffin isomerization reaction occurs rapidly at commercial operating temperatures. Thermodynamic equilibrium, however, slightly favors the isomers that are more highly branched. Because branched-chain isomers have a higher octane than straight-chain paraffins, this reaction improves product octane. Isomerization reactions are promoted by the acid function of the catalyst.

Isomerization of Paraffins and Naphthenes

$$R-C-C-C-C \rightleftharpoons R-C-\overset{\displaystyle C}{\underset{\displaystyle |}{C}}-C$$

$$\text{cyclopentane-R} \rightleftharpoons \text{cyclohexane-R'}$$
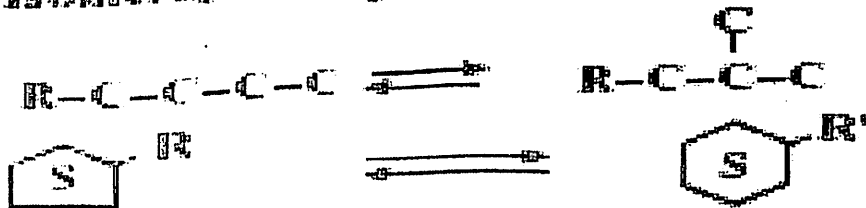
7.3. Dehydrocyclization of Paraffins:

The most-difficult Platforming reaction to promote is the dehydrocyclization of paraffins. This reaction consists of molecular rearrangement of a paraffin to a naphthene. Paraffin cyclization becomes easier with increasing molecular weight of the paraffin because the probability of ring formation increases. Partially offsetting this effect is the greater likelihood of the heavy paraffins to hydrocrack. Dehydrocyclization is favored by low pressure and high temperature and requires both the metal and acid functions of the catalyst.
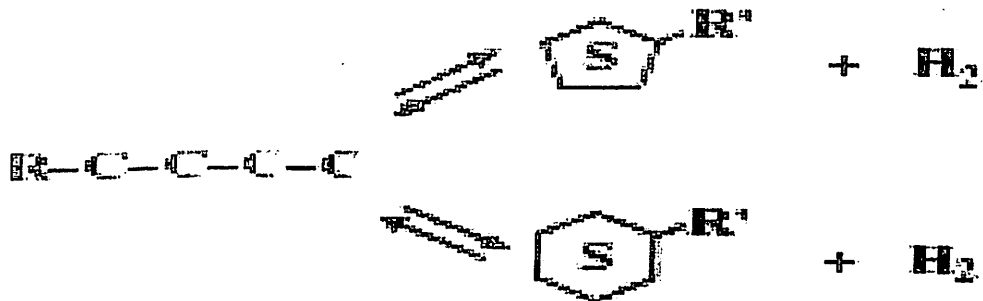
7.4. Hydrocracking and Dealkylation.

In addition to naphthene isomerization and paraffin cyclization reactions, the acid function catalyzes paraffin hydrocracking. Paraffin hydrocracking is favored by high temperature and high pressure. As paraffins crack and disappear from the gasoline boiling range, the remaining aromatics become concentrated in the product, thereby increasing product octane. However, hydrogen is consumed, and the net liquid product is reduced, making this reaction undesirable.

Dealkylation of aromatics includes both making the alkyl group (a side chain on the aromatic ring) smaller and removing the alkyl group completely. Examples are converting ethyl benzene to toluene and converting toluene to benzene, respectively. If the alkyl side chain is large enough, the reaction is similar to paraffin cracking. Dealkylation is favored by high temperature and high pressure.

$$R-C-C-C-C + H_2 \longrightarrow RH + C-C-C$$
with an H below the middle carbon.

Demethylation

$$R-C-C-C-C + H_2 \longrightarrow R-C-C-CH + CH_4$$

Benzene ring with R-C side chain $+ H_2 \longrightarrow$ benzene ring with RH $+ CH_4$

Dealkylation of Aromatics

Benzene ring with R side chain $+ H_2 \longrightarrow$ benzene ring with R' side chain $+ R''$

Symbol Key

Where pentagon with S, hexagon with S = Saturated Rings (Naphthenes)

hexagon with O = A Dehydrogenated Ring (Aromatic)
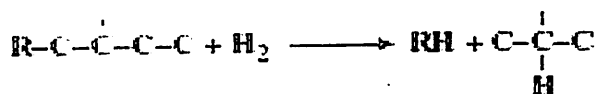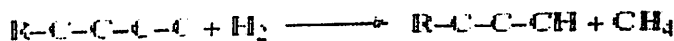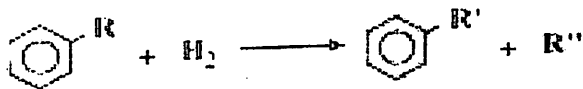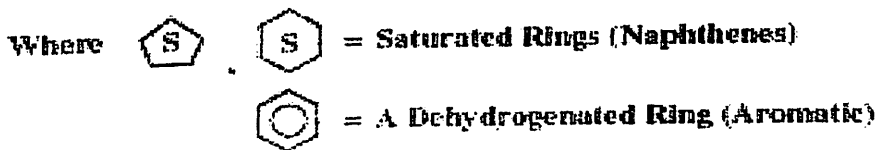
R, R', R'' = Radicals or Side Chains Attached to the Ring, for Example, —CH$_2$CH$_3$, an Ethyl Radical

7.5. Relative Reaction Rates

The primary reactions for the C6 and C7 paraffins proceed at vastly different rates. Because the hydrocracking rate for hexane is at least 3 times greater than the dehydrocyclization rate for hexane, only a small fraction of normal hexane is converted to aromatics. The rate of heptane dehydrocyclization is approximately 4 times that of hexane. Therefore, a substantially greater conversion of normal heptane to aromatics occurs than for hexane.

Reactions of naphthenes in the feedstock show significant differences between the alkylcyclopentanes and the alkylcyclohexanes. The alkylcyclopentanes react slowly and follow two competing' paths. The desired reaction is isomerization to an alkylcyclohexane followed by dehydrogenation to aromatics. The competing reaction is decyclization to form paraffins. In

contrast, the alkylcyclohexanes dehydrogenate rapidly and nearly completely to aromatics.

The relative ease of isomerization to an alkylcyclohexane increases with increasing carbon number. For example, the ratio of alkylcyclopentane isomerization rate to total alkylcyclopentane reaction rate is 0.67 for methylcyclopentane at low pressure. This ratio increases to 0.81 for dimethylcyclopentane, one carbon number higher.

The conversion of hydrocarbon types as a function of position in the catalyst bed for a moderate-severity Platforming operation is shown in Fig. 12 to 15.

Hydrocarbon-type profiles.
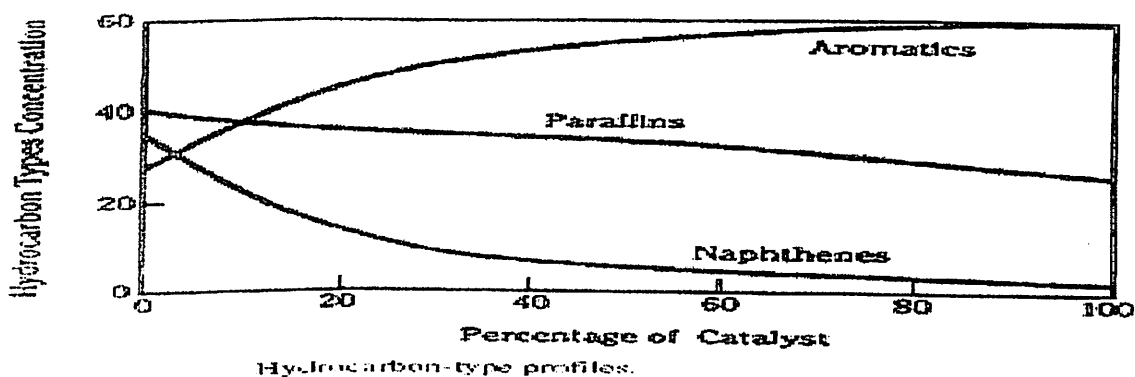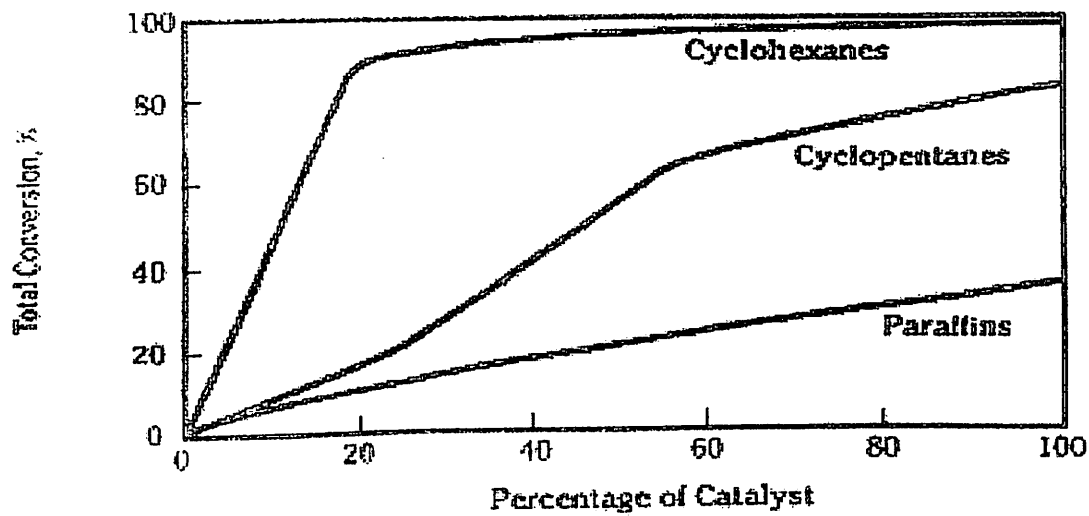
Figure 12

Reactant-type conversion profiles.

Figure 13
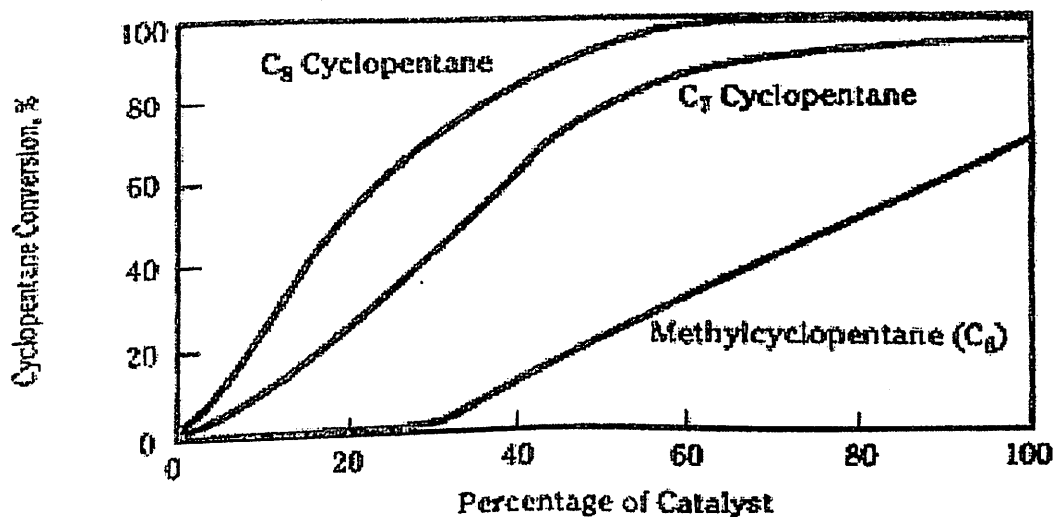
Cyclopentane conversion by carbon number.

Figure 14
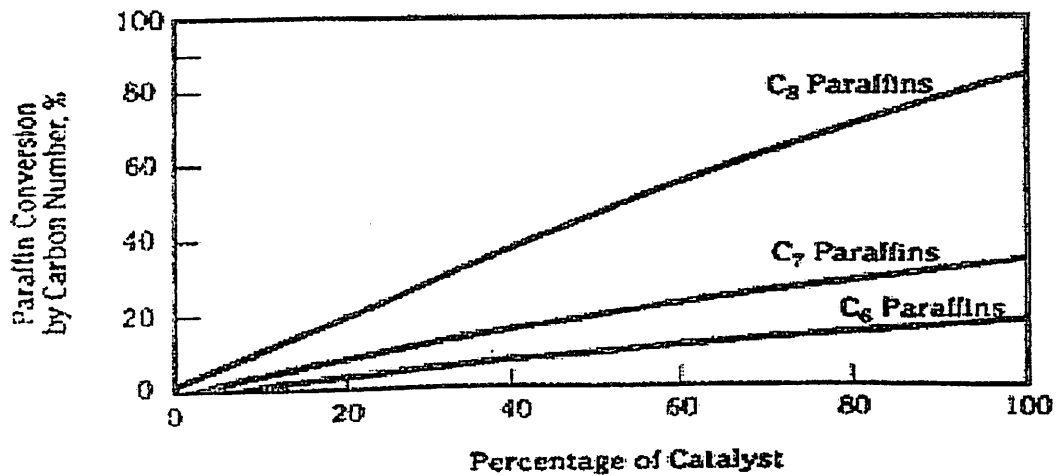
Paraffin conversion by carbon number.

Figure 15

The feedstock is a rich BTX naphtha with a paraffin, naphthenes, and aromatics (PNA) content of 42, 34, and 24 wt %, respectively. As the naphtha feed passes through the catalyst bed, total aromatics concentration increases and the concentration of naphthenes and paraffins decreases as they undergo conversion (Fig. 12). The high rate of conversion of cyclohexanes is shown by the rapidly decreasing concentration of naphthenes in the first 30 percent of the catalyst volume. The remaining naphthene conversion occurs at a slower rate and is indicative of cyclopentane conversion and dehydrocyclization of paraffins through a naphthene intermediate. By the reactor outlet, the naphthene concentration approaches a low steady-state value, which represents the naphthene intermediary present in the paraffin dehydrocyclization reactions. In contrast, paraffin conversion is nearly linear across the reactor bed.

Figure 13 illustrates the conversion of the three reactive species in the Platforming feedstock. The relative rates of conversion are markedly different. In the first 20 p~rcent of the catalyst, 90 percent of the cyclohexanes are converted, but conversion is only 15 percent for cyclopentanes and 10 percent for paraffins. Cyclopentanes are much less reactive than cyclohexanes. Figure 14 shows the relative reaction rate of cyclopentanes by carbon number.

Heavier components, which have a greater probability of isomerizing from a five- to six carbon ring, convert more readily than do the lighter components. The most difficult reaction, the conversion of paraffins, is characterized by carbon number in Fig. 15. As with the cyclopentanes, the heavier paraffins convert more readily than do the lighter paraffins. The relative ease of conversion associated with increasing carbon number for alkylcyclopentanes and paraffins explains why higher-boiling-range feedstocks are easier to process.

In summary, paraffins have the lowest reactivity and selectivity to aromatics and are the most difficult components to process in a Platforming unit. Although alkylcyclopentanes are more reactive and selective than paraffins, they still produce a significant amount of nonaromatic products. Alkylcyclohexanes are converted rapidly and quantitatively to aromatics and make the best reforming feedstock. As a general rule, heavier components convert more easily and selectively to aromatics than do the lighter components.

Heats of Reaction

Typical heats of reaction for the three broad classes of Platforming reactions are presented in Table 2. The dehydrocyclization of paraffins and dehydrogenation of naphthenes are endothermic. In commercial Platforming units, the majority of these reactions take place across the first two reactors, as indicated by the large negative-temperature differentials observed. In the final reactor, where a combination of paraffin dehydrocyclization and hydrocracking takes place, the net heat effect in the reactor may be slightly endothermic or exothermic, depending on processing conditions, feed characteristics, and catalyst.

TABLE 2 : Heats of Reaction

Heats of Reaction ΔH

Reaction	ΔH, kJ/mol H_2
Paraffin to naphthene	+44 (endothermic)
Naphthene to aromatic	+71 (endothermic)
Hydrocracking	−56 (exothermic)

CATALYSTS

Platforming catalysts are heterogeneous and composed of a base support material (usually Al2O3) on which catalytically active metals are placed. The first Platforming catalysts were monometallic and used platinum as the sole metal. These catalysts were capable of producing high-octane products; however, because they quickly deactivated as a result of coke formation on the catalyst, they required higher¬pressure, lower-octane Platforming operations.

As refiners needed greater activity and stability to move to lower pressure and higher octane, UOP introduced bimetallic catalysts in 1968. These catalysts contained platinum and a second metal, rhenium, to meet increasing severity requirements. Catalyst metals are typically added at levels of less than 1 wt % of the catalyst by using techniques that ensure a high level of metal dispersion over the surface of the catalyst. To develop the acid functionality of the catalyst, a promoter such as chloride or fluoride is added. Most catalyst development for SR Platforming has followed the path of maximizing the efficiency and balance of the metal and acid functionalities of the catalyst system.

The performance of UOP commercial fixed-bed catalysts is shown in Fig.16. The R¬86* catalyst, which was first commercialized in 2001, has become the preferred SR Platforming catalyst. Compared to the R-56* catalyst, R-86 provides a 1.0 LV % C5+ yield advantage and increased hydrogen yields while maintaining the same cycle length and excellent regenerability. The alumina base of R-86 has been reformulated, resulting in a lower-density support which provides lower coke make, reduced metals requirements, and reduced reload cost per reactor.
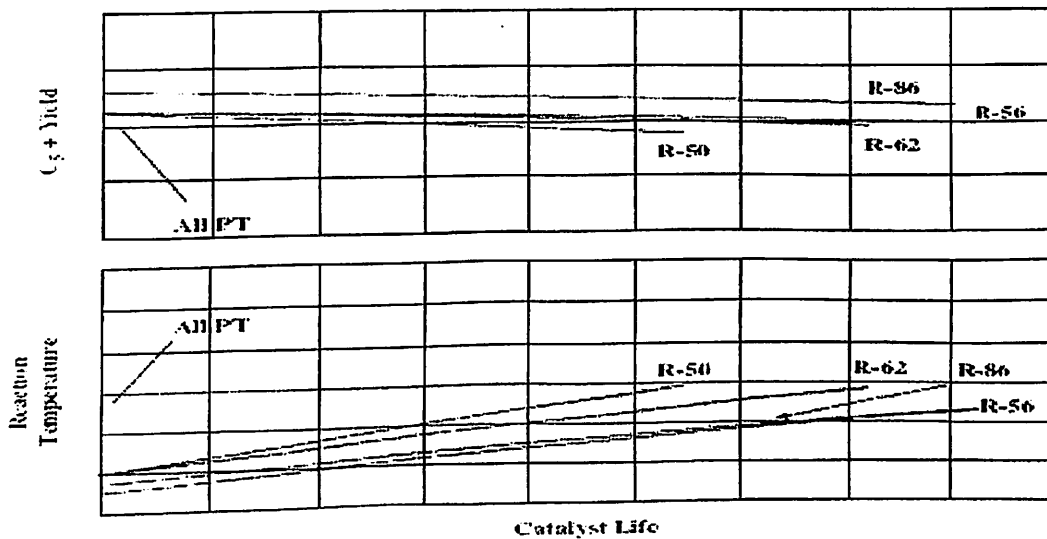
Performance summary of commercial fixed-bed UOP Platforming catalysts.

Figure 16

For cyclic reformers, UOP has developed a family of catalysts (both Pt-Re and pt only) based on the R~86 support that provides increased yields, high activity, and reduced coke make. Since cyclic reactors are sequentially taken off-line for regeneration, surface area stability is important as the number of regenerations increases. UOP is improving the R-86 support to further enhance the surface area stability to even higher levels, which will increase the catalyst life and reduce reload costs over time.

With the introduction of the UOP CCR Platforming process in 1971, Platforming catalyst development began a second parallel track to address the specific needs of the continuous process. The first UOP CCR Platforming unit used a conventional Pt-Re catalyst, but UOP quickly developed the R-30* series catalyst to provide higher yields of gasoline and hydrogen. Catalyst development for the CCR Platforming process has focused on the following areas:

- Lower coke production to reduce regenerator investment.
- Higher tolerance to multiple regeneration cycles to maximize catalyst life and minimize catalyst costs. Reducing the rate of surface area decline is important because reduced catalyst surface area increases

the difficulty of dispersing the metals on the catalyst surface and obtaining the optimum chloride level.

- High strength to reduce catalyst attrition in the unit.

- Metals optimization to reduce the platinum content of the catalyst and thus reduce the refinery working-capital requirement.

In 1992, UOP commercialized the R-130* CCR Platforming catalyst series with improved surface-area stability, activity, and strength compared to the R-30 series. The improved surface area stability of the R-130 alumina was achieved by modifying the alumina during formation, and it contains no additional components. Other CCR catalyst manufacturers obtain surface area stability by adding a component to the alumina. This method may result in a degradation of chloride retention which could decrease catalyst performance as the number of CCR cycles increases.

In 2000, UOP introduced the new R-200 catalyst series. Compared to the R-130 series, the R-200 series provides 30 percent less coke, up to 1.5 LV % higher C5+ yields, higher hydrogen yields, and improved strength with the same high surface area stability. The reduced coke make allows enhanced operating flexibility by allowing either high throughputs or higher-octane operations.

PROCESS VARIABLES

This section describes the major process variables and their effect on unit performance. The process variables are reactor pressure, reactor temperature, space velocity, hydrogen/ hydrocarbon (H2/HC) molar ratio, chargestock properties, catalyst selectivity, catalyst activity, and catalyst stability. The relationship between the variables and process performance is generally applicable to both SR and continuous regeneration modes of operation.

9.1. Reactor Pressure

The average reactor operating pressure is generally referred to as reactor pressure. For practical purposes, a close approximation is the last reactor inlet pressure. The reactor pressure affects reformer yields, reactor temperature requirement, and catalyst stability. Reactor pressure has no theoretical limitations, although practical operating constraints have led to a historical range of operating pressures from 345 to 4830 kPa (50 to 700 lb/in2 gage). Decreasing the reactor pressure increases hydrogen and reformate yields, decreases the required temperature to achieve product quality, and shortens the catalyst cycle because it increases the catalyst coking rate. The high coking rates associated with lower operating pressures require continuous catalyst regeneration.

9.2. Reactor Temperature

The primary control for product quality in the Platforming process is the temperature of the catalyst beds. By adjusting the heater outlet temperatures, a refiner can change the octane of the reformate and the quantity of aromatics produced.

The reactor temperature is usually expressed as the weighted-average inlet temperature (WAIT), which is the summation of the product of the fraction of catalyst in each reactor multiplied by the inlet temperature of the reactor, or as the weighted-average bed temperature (WABT), which is the summation of

the product of the fraction of catalyst in each reactor multiplied by the average of its inlet and outlet temperatures. Temperatures in this chapter refer to the WAIT calculation. Typically, SR Platforming units have a WAIT range of 490 to 525°C (914 to 977°F). CCR Platforming units operate at a WAIT of 525 to 540°C (977 to 1004°F).

9.3. Space Velocity

Space velocity is defined as the amount of naphtha processed over a given amount of catalyst over a given length of time. The space velocity is an indication of the residence time of contact between reactants and catalyst. When the hourly volume charge rate of naphtha is divided by the volume of catalyst in the reactors, the resulting quotient, expressed in units of h-1, is the liquid hourly space velocity (LHSV). Alternatively, if the weight charge rate of naphtha is divided by the weight of catalyst, the resulting quotient, also expressed in units of h-1, is the weighted hourly space velocity (WHSV). Although both terms are expressed in the same units, the calculations yield different values. Whether LHSV or WHSV is used depends on the customary way that feed rates are expressed in a given location. Where charge rates are normally expressed in barrels per stream day, LHSV is typically used. Where the rates are expressed in terms of metric tons per day, WHSV is preferred.

Space velocity together with reactor temperature determines the octane of the product. The greater the space velocity, the higher the temperature required to produce a given product octane. If a refiner wishes to increase the severity of a reformer operation, she or he can either increase the reactor temperature or lower the space velocity. A change in space velocity has a small impact on product yields when the WAIT is adjusted to maintain constant severity. Higher space velocities may lead to slightly higher yields as a result of less time available in the reactors for dealkylation reactions to take place. This advantage is partially offset by the higher rate of hydrocracking reactions at higher temperatures.

9.4. Hydrogen/Hydrocarbon Molar Ratio

The H2/HC ratio is the ratio of moles of hydrogen in the recycle gas to moles of naphtha charged to the unit. Recycle hydrogen is necessary to maintain catalyst-life stability by sweeping reaction products from the catalyst. The rate of coke formation on the catalyst is a function of the hydrogen partial pressure.

An increase in the H2/HC ratio increases the linear velocity of the combined feed and supplies a greater heat sink for the endothermic heat of reaction. Increasing the ratio also increases the hydrogen partial pressure and reduces the coking rate, thereby increasing catalyst stability with little effect on product quality or yields. Directionally, lower H2/HC ratios provide higher C5+ and hydrogen yields, although this benefit is difficult to measure in commercially operating units.

9.5. Chargestock Properties

The boiling range of Platforming feedstock is typically about 100°C (212°F) to 180°C (356°F). Chargestocks with a low initial boiling point (IBP), less than 75°C (16rF) measured according to American Society for Testing and Materials specification ASTM D-86, generally contain a significant amount of C5 components which are not converted to valuable aromatics products. These components dilute the final product, thus requiring a higher severity to achieve an equivalent product octane. For this reason, feedstocks are generally C6+ naphthas. The endpoint of the chargestock is normally set by the gasoline specifications for the refinery with the realization that a significant rise in endpoint, typically 15 to 25°C (27 to 45°F), takes place between the naphtha charge and reformate product. The effect of hydrocarbon types in the chargestock on aromatics yield was discussed in the "Process Chemistry" section and can be further illustrated by examining a broad range of chargestock compositions. Licensers typically develop a large database of feedstock's that have been analyzed and tested under controlled conditions to characterize expected reforming yields over a range of octanes. This database allows yields to be predicted for future chargestocks of known

composition. Four chargestocks of widely varying compositions were chosen from such a database and are summarized in Fig. 17.

P = Paraffin
N = Naphthene
A = Aromatics

Naphtha characterization by hydrocarbon type.
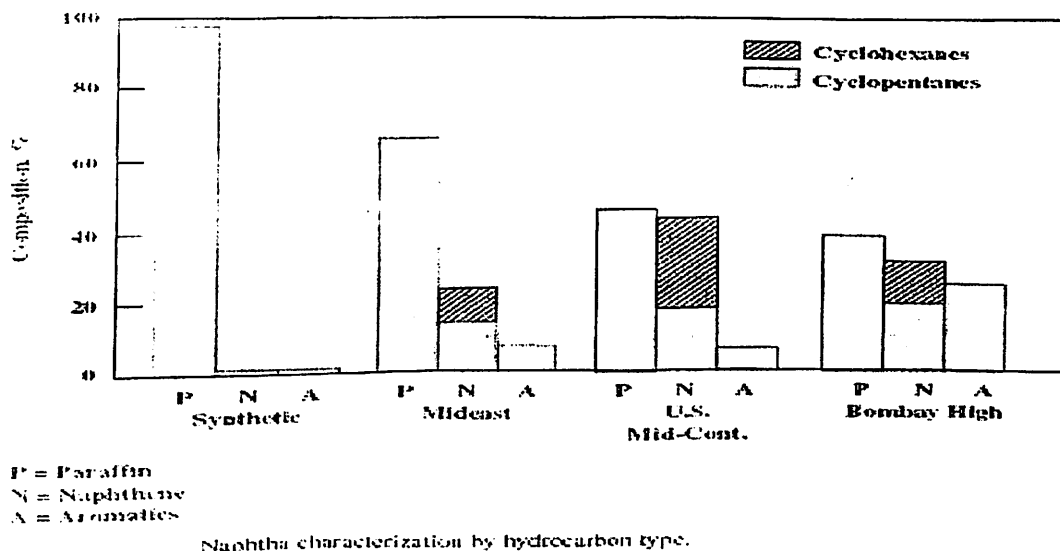
Figure 17

The chargestock range chosen covers lean through rich feeds. The aromatics plus cyclohexanes content is a measure of their ease of conversion, and the paraffins plus cyclopentanes content indicates the difficulty of reforming reactions. The effect of feedstock composition on aromatics yield is shown in Fig. 18. Increasing conversion leads to an increase in the total yield of aromatics for each of the feedstocks. Feeds that are easier to process produce the highest yield of aromatics at any level of conversion.

Feedstock conversion and aromatics yield.
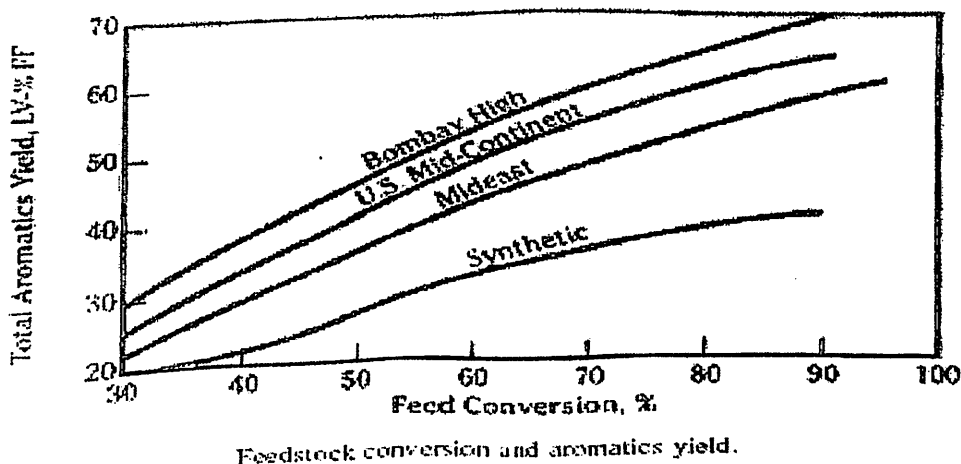
Figure 18

9.6 Catalyst Selectivity

Catalyst selection is usually tailored to the refiner's individual needs. A particular catalyst is typically chosen to meet the yield, activity, and stability requirements of the refiner. This customization is accomplished by varying basic catalyst formulation, chloride level, platinum content, and the choice and quantity of any additional metals. Differences in catalyst types can affect other process variables. For example, the required temperature to produce a given octane is directly related to the type of catalyst. Catalyst selectivity can be easily described as the amount of desired product that can be yielded from a given feedstock. Usually, the selectivity of one catalyst is compared with that of another. At constant operating conditions and feedstock properties, the catalyst that can yield the greatest amount of reformate at a given octane in motor fuel applications or the greatest amount of aromatics in a BTX operation has the greatest selectivity.

9.7. Catalyst Activity and Stability

Activity is the ability of a catalyst to promote a desired reaction with respect to reaction rate, space velocity, or temperature. Activity is also expressed in a relative sense in that one catalyst is more active than another. In motor fuel applications, activity is generally expressed as the temperature required to produce reformate at a given octane, space velocity, and pressure. A more active catalyst can produce reformate at the desired octane at a lower temperature.

Activity stability is a measure of the rate at which the catalyst deactivates over time. In semiregenerative reforming, stability is an indication of how long the catalyst can remain in operation between regenerations. In CCR Platforming, stability is an indication of how much coke will be formed while processing a given feed at a given severity, which, in turn, determines the size of the catalyst regeneration section.

10.3. DESCRIPTION OF THE PROCESS FLOW FOR CCR REORMING

The principal products from the aromatics complex illustrated in Fig. 20 are benzene, para-xylene, and ortho-xylene. If desired, a fraction of the toluene and C9 aromatics may be taken as products, or some of the reformate may be used as a high-octane gasoline blending component. The naphtha is first hydrotreated to remove sulfur and nitrogen compounds and then sent to a CCR Platforming unit, where paraffins and naphthenes are converted to aromatics. This unit is the only one in the complex that actually creates aromatic rings. The other units in the complex separate the various aromatic components into individual products and convert undesired aromatics into dditional high-value products. The CCR Platforming unit is designed to run at high severity, 104 to 106 research octane number, clear (RON C), to maximize the production of aromatics. This high-severity operation also extinguishes virtually all nonaromatic impurities in the C8+ fraction of the reformate, thus eliminating the need for extraction of the C8 and C9 aromatics. The reformate product from the CCR Platforming unit is sent to a debutanizer column within the Platforming unit to strip off the light ends.

The reformate from the CCR Platforming unit is sent to a reformate splitter column. The $C7^+$ fraction from the overhead is sent to the Sulfolane unit for extraction of benzene and toluene. The Ca + fraction from the bottom of the reformate splitter is clay-treated and then sent directly to the xylene recovery section of the complex.

The Sulfolane unit extracts the aromatics from the reformate splitter overhead and rejects a paraffinic raffinate stream. The aromatic extract is clay-treated to remove trace olefins. Then individual high-purity benzene and toluene products are recovered in the benzene-toluene (8T) fractionation section of the complex. The C8+ material from the bottom of the toluene column is sent to the xylene recovery section of the complex. The raffinate from the Sulfolane unit may be further refined into paraffinic solvents, blended into gasoline, used as feedstock for an ethylene plant, or converted to additional benzene by an RZ-100* Platforming unit.

Toluene is usually blended with C9 and C10 aromatics (A9+) from the overhead of the A9 column and charged to a Tatoray unit for the production of additional xylenes and benzene. The effluent from the Tatoray unit is sent to a stripper column within the Tatoray unit to remove light ends. After the effluent is clay-treated, it is sent to the BT fractionation section, where the benzene product is recovered and the xylenes are fractionated out and sent to the xylene recovery section. The overhead material from the Tatoray stripper or THDA stripper column is separated into gas and liquid products. The overhead gas is exported to the fuel gas system, and the overhead liquid is normally recycled to the CCR Platforming debutanizer for recovery of residual benzene.

Instead of feeding the toluene to Tatoray, another processing strategy for toluene is to feed it to a para-selective catalytic process such as PX-Plux, where the para¬xylene in the xylene product is enriched to 85% and cyclohexane-grade benzene is coproduced. The concentrated para-xylene product could then be easily recovered in a single-stage crystallization unit. In such a case, the Cg + aromatics could be fed to a Toray TAC9 unit and converted predominantly to mixed xylenes.

The C8+ fraction from the bottom of the reformate splitter is clay-treated and then charged to a xylene splitter column. The xylene splitter is designed to rerun the mixed xylenes feed to the Parex unit down to very low levels of A9 concentration. The A9 builds up in the desorbent circulation loop within the Parex unit, and removing this material upstream in the xylene splitter is more efficient. The overhead from the xylene splitter is charged directly to the Parex unit. The bottoms are sent to the A9 column, where the A9 fraction is rerun and then recycled to the Tatoray or THDA unit. If the complex has no Tatoray or THDA unit, the A9+ material is usually blended into gasoline or fuel oil.

If ortho-xylene is to be produced in the complex, the xylene splitter is designed to make a split between meta- and ortho-xylene and drop a targeted amount of ortho-xylene to the bottoms. The xylene splitter bottoms are then

sent to an o-X column where high-purity ortho-xylene product is recovered overhead. The bottoms from the o-X column are then sent to the A9 column.

The xylene splitter overhead is sent directly to the Parex unit, where 99.9 wt % pure paraxylene is recovered by adsorptive separation at 97 wt % recovery per pass. Any residual toluene in the Parex feed is extracted along with the para-xylene, fractionated out in the finishing column within the Parex unit, and then recycled to the Tatoray or THDA unit. The raffinate from the Parex unit is almost entirely depleted of para-xylene, to a level of less than 1 wt %. The raffinate is sent to the Isomar unit, where additional para-xylene is produced by re establishing an equilibrium distribution of xylene isomers. Any ethylbenzene in the Parex raffinate is either converted to additional xylenes or dealkylated to benzene, depending on the type of Isomar catalyst used. The effluent from the Isomar unit is sent to a deheptanizer column. The bottoms from the deheptanizer are clay-treated and recycled back to the xylene splitter. In this way, all the C8 aromatics are continually recycled within the xylene recovery section of the complex until they exit the aromatics complex as para-xylene, ortho-xylene, or benzene. The overhead from the deheptanizer is split into gas and liquid products. The overhead gas is exported to the fuel gas system, and the overhead liquid is normally recycled to the CCR Platforming debutanizer for recovery of residual benzene.

Within the aromatics complex, numerous opportunities exist to reduce overall utility consumption through heat integration. Because distillation is the major source of energy consumption in the complex, the use of cross-reboiling is especially effective. This technique involves raising the operating pressure of one distillation column until the condensing distillate is hot enough to serve as the heat source for the reboiler of another column. In most aromatics complexes, the overhead vapors from the xylene splitter are used to reboil the desorbent recovery columns in the Parex unit. The xylene splitter bottoms are often used as a hot-oil belt to reboil either the Isomar deheptanizer or the Tatoray stripper column. If desired, the convection section of many fired heaters can be used to generate steam.

10.4. FEEDSTOCK CONSIDERATIONS

Any of the following streams may be used as feedstock to an aromatics complex:

- Straight-run naphtha
- Hydrocracked naphtha
- Mixed xylenes
- Pyrolysis gasoline (pygas)•
- Coke-oven light oil
- Condensate
- Liquid petroleum gas (LPG)

Petroleum naphtha is by far the most popular feedstock for aromatics production. Reformed naphtha, or reformate, accounts for 70 percent of total world BTX supply. The pygas by-product from ethylene plants is the next-largest source at 23 percent. Coal liquids from coke ovens account for the remaining 7 percent. Pygas and coal liquids are important sources of benzene that may be used only for benzene production or may be combined with reformate and fed to an integrated aromatics complex. Mixed xylenes are also actively traded and can be used to feed a stand¬alone Parex-Isomar loop or to provide supplemental feedstock for an integrated complex.

Condensate is a large source of potential feedstock for aromatics production. Although most condensate is currently used as cracker feedstock to produce ethylene, condensate will likely play an increasingly important role in aromatics production in the future.

Many regions of the world have a surplus of low-priced LPG that could be transformed into aromatics by using the new UOP-BP Cyclar* process. In 1999 the first Cyclar-based aromatics complex started up in Saudi Arabia. This Cyclar unit is integrated with a downstream aromatics complex to produce para-xylene, ortho¬xylene, and benzene.

Pygas composition varies widely with the type of feedstock being cracked in an ethylene plant. Light cracker feeds such as liquefied natural gas (LNG) produce a pygas that is rich in benzene but contains almost no ca aromatics. Substantial amounts of Ca aromatics are found only in pygas from ethylene plants cracking naphtha and heavier feedstocks. All pygas contains significant amounts of sulfur, nitrogen, and dienes that must be removed by two-stage hydrotreating before being processed in an aromatics complex.

Because reformate is much richer in xylenes than pygas, most para-xylene capacity is based on reforming petroleum naphtha. Straight-run naphtha is the material that is recovered directly from crude oil by simple distillation. Hydrocracked naphtha, which is produced in the refinery by cracking heavier streams in the presence of hydrogen, is rich in naphthenes and makes an excellent reforming feedstock but is seldom sold on the merchant market. Straight-run naphthas are widely available in the market, but the composition varies with the source of the crude oil. Straight-run naphthas must be thoroughly hydrotreated before being sent to the aromatics complex, but this pretreatment is not as severe as that required for pygas. The CCR Platforming units used in BTX service are run at a high-octane severity, typically 104 to 106 RONC, to maximize the yield of aromatics and eliminate the nonaromatic impurities in the Ca + fraction of the reformate.

Naphtha is characterized by its distillation curve. The cut of the naphtha describes which components are included in the material and is defined by the initial boiling point (IBP) and endpoint (EP) of the distillation curve. A typical BTX cut has an IBP of 75°C (165°F) and an EP of 150°C (300°F). However, many aromatics complexes tailor the cut of the naphtha to fit their particular processing requirements.

An IBP of 75 to 80°c (165 to 175°F) maximizes benzene production by including all the precursors that form benzene in the reforming unit. Prefractionating the naphtha to an IBP of 100 to 105°C (210 to 220°F) minimizes the production of benzene by removing the benzene precursors from the naphtha.

If a UOP Tatoray unit is incorporated into the aromatics complex, Cg aromatics become a valuable source of additional xylenes. A heavier naphtha with an EP of 165 to 170°C (330 to 340°F) maximizes the C9 aromatic precursors in the feed to the reforming unit and results in a substantially higher yield of Xylenes or para-xylene from the complex. Without a UOP Tatoray unit, C9 aromatics are a low-value byproducts from the aromatics complex that must be blended into gasoline or fuel oil. In this case, a naphtha EP of 150 to 155°C (300 to 310°F) is optimum because it minimizes the C9 aromatic precursors in the reforming unit feed. If mixed xylenes are purchased as feedstock" for the aromatics complex, they must be stripped, clay treated, and rerun prior to being processed in the Parex-Isomar loop.

10.5. A SAMPLE CASE STUDY

An overall material balance for a typical aromatics complex is shown in Table 1 along with the properties of the naphtha feedstock used to prepare the case. The feedstock is a common straight-run naphtha derived from Arabian Light crude. The configuration of the aromatics complex for this case is the same as that shown in Fig. 2 except that the o-X column has been omitted from the complex to maximize the production of para-xylene. The naphtha has been cut at an endpoint of 165°C (330°F) to include all the C9 aromatic precursors in the feed to the Platforming unit.

TABLE 3

Overall Material Balance

Naphtha feedstock properties	
Specific gravity	0.7347
Initial boiling point, °C (°F)	83 (181)
Endpoint, °C (°F)	166 (331)
Paraffins/naphthenes/aromatics, vol %	66/23/11

Overall material balance, kMTA*	
Naphtha	940
Products	
Benzene	164
para-Xylene	400
C_{10} + aromatics	50
Sulfolane raffinate	140
Hydrogen-rich gas	82
LPG	68
Light ends	36

*MTA — metric tons per annum.

10.6. CONCLUSION

Aromatics production can be substantially increased using Reforming technology as compared to other available technologies. Aromatic production can be maximized in a reforming unit by high severity operations which promote specific reactions leading to high aromatic production, particularly BTX (Benzene, Toulene and mixed Xylenes). Modifications can be made to the standard aromatics complex leading to promotion of a specific aromatic compound, thus increasing selectivity and production of aromatics which are required for making high octane fuels

11.3. CATALYST ACTIVITY

The WAIT requirement to meet a given Gs + RONG is obviously affected by many things. At the outset of a run with fresh catalyst, one would expect that the WAIT required would only be affected by the feed character, RONG desired, feed rate, and catalyst type. However, things are not this simple. An operational upset could occur which will effect the water- chloride balance and the apparent catalyst activity will change.

There is a calculation procedure for estimating the start-of-run (SOR) WAIT requirement. This SOR WAIT is the temperature at which a fresh catalyst loading would operate in order to produce a certain RONG from a feed characterized by a certain N and A content and charged at a given LHSV. There are at least two important ways at which this estimate can be put to use:

i. GGR Platforming Unit WAIT target at start-up.

ii. GGR Platforming Unit Delta WAIT (predicted SOR WAIT minus actual WAIT) for tracking catalyst activity with respect to regeneration cycles.

The first use, (i), is fairly straightforward. The calculation enables the process engineer or supervisor to estimate the WAIT required to meet product requirements.

For Number (ii), the basic idea is to determine a number (Delta WAIT) which puts the catalyst temperature requirement on a consistent or normalized basis for comparing day-to-day operation. This would not be necessary; of course, if the Platforming Unit ran at the same conditions (feed N and A, RONG, LHSV) all the time. Of course, this is seldom the case.

What Delta WAIT does, then, is normalize Reactor temperature data with respect to Platforming feed N and A, RONG and LHSV. It is defined as the difference between the WAIT the CCR Platforming Unit is operating at, given the three parameters above, and the fresh catalyst WAIT requirement for the

same parameters. It is the activity difference between the real catalyst and fresh catalyst.

Tabulation or graphical plotting of Delta WAIT is a natural follow-up. In maintaining a plot, the engineer can monitor the effects of operating changes made to remedy a catalyst activity problem due to, for instance, a feed sulfur upset. In this case, delta WAIT can be plotted versus regeneration cycles. It probably would take a few catalyst regeneration cycles for the catalyst activity to get back to normal, so on a day-to-day basis, the engineer can track the improvement in activity. Disruptions in and recovery of the water-chloride balance can also be tracked using the Delta WAIT calculation and plot.

The SOR WAIT requirement calculation is now explained. The figures used are not meant to cover all the variables, which can affect the apparent fresh catalyst activity. Predictions of the SOR WAIT requirements from the figures should, however, be within plus or minus 3°C (5°F) of the actual requirement.

11.4. Catalyst Selectivity

Selectivity is defined as the tendency of a given catalyst and the operation of that catalyst to produce the desired material. In most Platforming operations, the most desired material is reformate or more specifically the yield of C5+ liquid. The product quality will be defined as C5+ RONC, the research octane number clear.

The selectivity of a Platforming catalyst and operation is dependent upon several variables. The effects of Platforming feedstock characteristics (N and A content, 50% boiling point and end boiling point), product quality (RONC), and average Reactor pressure on selectivity to C5+ liquid is discussed.

There are two sets of four selectivity curves. One set is for full-boiling-range naphthas, which are generally defined as having an initial boiling point of 82°C (180°F) and an end boiling point in the range of 176~204°C (350-400°F). The other set of curves is for light- boiling-range naphthas which have an end boiling point less than 176°C (350°F).

OPTIMIZATION OF COMMERCIAL REFORMERS

INTRODUCTION:

Business decisions on commercial catalytic reformers are based on information provided from process data and laboratory analyses. To enable the refiner to maximize the effectiveness of readily available process data, techniques are persisted for collection of raw process data, determining the validity of the data, and conversion of the data into usable information via a process simulation model. Once a catalytic reformer is accurately modeled, business decisions can be made with respect to catalyst performance, product yields, mechanical or process changes in the system, and control and optimization of the catalytic reforming process.

TEST RUNS

Objective of a test run is to measure the performance of a process unit. In the case of a catalytic reformer, a test run can be used to measure the performance of both mechanical equipment and the reforming catalyst. A successful test run is predicated on six basic issues:

I. Identification of test runs objective(s)

2. Proper selection of streams to be crossed by the material and energy balance envelope.

3. Steady-state operation

4. Accurate process measurements of flows, temperatures, and

   Pressures.

5. Correct sample collection

6. Coordination between process engineering, unit operations,

   Refinery planning, and the laboratory.

The cost of performing routine test runs is insignificant in comparison with the lost opportunity cost of not having valid information for making business decisions.

A. Test Run Objectives

Test run objectives must be identified prior to defining data collection requirements and specifying test run operating conditions.; Identifying the test run objectives and designing a test run to meet those objectives will minimize the data collection and laboratory test requirements and the disruption of refinery operations.

B. Material and Energy Balance Envelope

Once the test run objective has been identified, the test run material and energy balance envelope can be defined. This definition includes identifying the process measurements to be recorded and the samples to be collected for the test run. This envelope varies from one catalytic reformer unit to another normally includes the feed preheat section, reactor section, product separator and fractionators. The material and energy balance envelope should include as few pieces of process equipment as needed to meet the test run objectives, should cross as few process streams as possible, and must cross only process and utility lines that can be accurately measured and sampled using the instrumentation and sample points available. A line containing two-phase flow can not he crossed by the material and energy balance envelope; neither can a line without a flow meter with corresponding temperature and pressure indications a sample collection point. Care should be taken to avoid process condition a line that will affect the measuring instrumentation or the sample collection such as using an orifice plate as the primary flow measuring clement when the process stream being measured is at its bubble point.

C. STEADY –STATE OPERATIONS

. It is important to have the unit in steady –state operations at the time of the test run. Steady –state operations can be determined by monitoring the standard Deviations of various process variables on a once –per minute basis for 30 minutes.

Variables to be checked and the desired allowable standard deviations for each variables .If any variables exceeds the standard deviation specification, the unit is not in steady state. A program can easily be installed in a

distributed control system (DCS) to generate the date required to determine control s a steady-state operation.

D. PRECISE FLOW MEASUREMENT

The major sources of errors in most refinery test runs are feed and product flow measurement. Commercial catalytic reformer units uses orifice plates as the primary flow measurements elements. To minimize flow errors it is recommended that the orifice diameter of each orifice plate be verified at each unit turnaround and any orifice plates that exhibit wear be replaced at that time. Approximately 2 weeks before the test run different pressure elements for each flowmeter should be zeroed and spanned ,During the week preceding the test run,daily material balance should be performed to verify the foments calibration before doing the test run.,If feed and or produce thanks are available ,meter readings should be compared to change in tank inventions.

E.CORRECT SAMPLE COLLECTION

Refinery laboratories are often criticized unfairly for reporting erroneous results when in fact problems are. often not in the analysis performed but rather in the technique and/or equipment used for the sample collection. For example, one common problem is caused when reformate is sampled from the reformate run-down line. The same is collected at flowing temperature in a glass sample bottle and taken to the laboratory to be tested for research octane number clear (RONC), Reid vapor pressure (RVP), gravity, and component analysis by, gas chromatography (GC). If the sample is drawn directly from the run-down, line into a simple container, a small amount of the butane (maybe 0.5 % of the total sample) can flash while the sample container is being filled. Because the blending octane number of the flashed sample is very close to that of the reformate and the RONC test procedure is known to have a wide variation in reported results, the reported RONC is not questioned. Likewise, the gravity analysis is not questioned because the small quantity of butane flashed does not change the gravity of the reformate beyond what is expected. The GC analysis reports 50 to 75 % of the expected

butane concentration, and the fault is placed on the laboratory for a "bad" GC analysis when in reality it was a sample collection errors.

F. PLANING COORDINATION

Coordination between process engineering, unit operations, refinery planning. and the laboratory is critical to a successful test run. Because a test run is performed for process engineering, the process engineering group has the responsibility for the coordination. The key issue in coordinating a test run is finding a point in time at which the feedstock needed for the test run will be in adequate supply to allow steady-state operations and the unit operating conditions can be changed to meet the test run requirements. If the required unit operating conditions include a specific octane severity or a number of severities, this must be coordinated with the refinery planning department to avoid causing problems in product blending and shipping. Once a time has been found that will meet feed and severity requirements, coordination must be arranged with unit operations for proper unit staffing and to minimize disturbances from outside sources. For example, maintenance work should be minimized during the test run. The net effect of properly planning and executing a test run is the development of reliable data for refinery decision making at a minimum cost for data collection and analysis.

DATA RELIABILITY

In many areas of business and commerce, subjective units of measure such as good, fair, and bad are used to describe the quality of products, systems, and measurements. Refinery engineers require a much more objective self of standards define the quality of data used in process modeling. Precisely defined te.-nlS of accuracy and precision are used to describe the quality of data.

ACCURACY AND PRECISION

Accuracy is defined as the closeness between a reported measured varible and the variable's true value or accepted standard. For example, if the true specific gravity of a stream is 0.750 and the gravity measured and reported by

a laboratory is 0.754, the accuracy would be reported as +0.004. The reproducibility of a measurement under controlled conditions is referred to as precision (2). With sufficient testing, using the same test procedure, statistical precision terms of repeatability and reproducibility can be established.

OPTIMIZATION OF REFORMERS WITH MATERIAL BALANCE:

DATA VERIFICATION:

Refiners must make the best use of the data available when making business decisions. Because the data values available from process measurements and laboratory tests are not going to be true values, techniques must be developed to determine the overall validity of the reported data. The following procedures outline tests that can be made on catalytic reformer stream flow and composition measurements to verify the overall data accuracy. Some of the tests are subjective and are meant only to identify obvious problems with data presented. Other tests are objective and must meet specific closures. If all tests pass the requirements, it can be concluded that the measured stream flow and composition data are valid.

Material Balance

The material balance on reformer test run data should close within + 1.0 wt %. A spreadsheet is used to simplify calculations. It is recommended that all extraneous streams entering the material balance that do not go through the reactor section be treated as negative products. This will result in the individual component yields being calculated on a reactor system outlet basis. The material balance error is defined by the following equation:

Material balance error = (weight feed − weight products) x 100 \ weight feed

Spreadsheet calculations shows the material balance for the sample case data to be 0.017% which is within the + 1 % closure specification. The values for all streams crossing the material balance are provided.

A common mistake when evaluating test run data is to normalize reformer product flows to close the material balance. This practice skews all data and serves to mask a real data problem. When the material balance data are not normalized, quite often it is simple to identify the source of the error.

B. Hydrogen Balance

The hydrogen balance is calculated by adding the weight of hydrogen in each stream to determine the total amount of hydrogen in the feed and products. The hydrogen balance error should not exceed + 0.5 %. The hydrogen balance error is defined as

Hydrogen error = $\dfrac{\text{(wt. feed hydrogen} - \text{wt. product hydrogen)} * 100}{\text{Wt feed hydrogen}}$

The hydrogen balance can be calculated quite quickly in a spreadsheet. The weight of hydrogen in a stream can be calculated by summing the weight of hydrogen contributed by each component using the following : The weight of hydrogen contributed by component C_iH_j>is equal to the weight of the stream multiplied by the weight fraction of C_iH_i times a factor HFACTOR.

HFACTOR = $\dfrac{J * \text{atomic wt. of hydrogen}}{j * \text{atomic wt. of hydrogen} + i * \text{atomic wt. of carbon .}}$

In the sample test run data the hydrogen to balance was 0.46% This is well within the 0.5% criterion for acceptable data.

STREAM	FEED	Net gas	Stabilizer o/H gas	Stabilizer o/H liquid	Reformate	HFACTOR
FLOW KG/h	47636	2444	137	4276	40771	
WEIGHT%						
H2	0	92.45	67.22			1
C1	0	3.24	7.05	0.12		0.25
C2	0	1.99	9.47	5.24		0.2
C3	0	1.43	9.32	20.55		0.1818
I-C4	0	0.35	2.37	12.14	0.06	0.1724
n-c4	0	0.27	0.27	17.34	0.29	0.1724
P5	1.93	0.22	2.16	38.18	1.4	0.1667
P6	9.57	0.05	0.2	5.38	13.89	0.1628
P7	12.16			0.12	9.89	0.16
P8	13.07				7.85	0.1579
P9	5.23				1.95	0.1562
P10	1.18				0.18	0.1549
P11	0.13					0.1538
MCP	3.66				1.78	
CH	3.69				0.2	
N7	13.13				1.71	0.1429
N8	11.95				0.9	0.1429
N9	10.08				0.25	0.1429
N10	2.4				0.04	0.1429
N11	0.32					0.1429
A6	0.59				5.31	0.0769
A7	2.37				18.13	0.0968
A8	4.31				21.8	0.1028
A9	2.8				11.31	0.1074
A10	0.9				0.24	
A11	0.01				0.24	

H2 IN FEED	H2 IN Net gas	H2 IN Stabilizer o/H gas	H2 in Stabilizer O/H liquid	H2 in Reformate
0	2259.478	92.0914	0	0
0	19.7964	2.414625	1.2828	0
0	9.72712	2.59478	44.81248	0
0	6.35376456	2.32129512	159.7509324	0
0	1.4747096	0.55976556	89.49394336	4.21735224
0	1.13763312	0.06377076	127.8274282	20.38386916
153.25978	0.89631256	0.49329864	272.1505526	95.1513598
742.16697	0.1989416	0.0446072	37.45194464	921.9513613
926.80602	0	0	0.820992	645.160304
983.08938	0	0	0	505.3626607
389.15087	0	0	0	124.1843889
87.070034	0	0	0	11.36777022
9.5243418	0	0	0	0
0	0	0	0	0
0	0	0	0	0
893.78331	0	0	0	99.62760789
813.45854	0	0	0	52.4355831
686.16419	0	0	0	14.56543975
163.37243	0	0	0	2.33047036
21.78299	0	0	0	0
21.61293	0	0	0	166.4838937
109.28461	0	0	0	715.5245266
211.05987	0	0	0	913.6944184
143.25098	0	0	0	495.2428907
	0	0	0	0
	0	0		0
		0		0
		0		
		0		
		0		

C. Cyclic Ring Balance

The knowledge that the relative rate of cyclization of paraffins to naphthenes and aromatics increase approximately linearly with carbon number and that the relative rate of paraffin cracking increase nearly linearly with carbon number allows the use of increase in ring compounds to check for errors in the feed and reformate analysis (9-11). The number of rings in the feed and reformate for each carbon number is calculated by adding the moles of naphthenes and aromatics by carbon number. The relative increase can then be calculated by calculating a percentage change in the rings for each carbon number. This is simply the difference in feed and product rings divided by the feed rings by carbon number and multiplied by 100. If the cracking reactions did not occur, a plot of the percent increase in rings versus carbon number would yield a nearly straight line, But, because the reformer catalyst is bifunctional and cracking does occur and increase significantly with C9 + compounds, the theoretical linear plot shifts to a function that is increasing through C8 or C9 followed by a drastic change in slope. Table shows the calculated rings for the sample case feed and reformate streams. Spreadsheet shows typical plot of the percent increase in rings. The loss of C6 rings is typical at the sample plot of the sample case feed and reformate streams. Figure 1 is a typcial plot of the the percent increase in rings. The loss of C6 rings is typical at the sample unit operating pressure and severity. If either the pressure is decreased or the severity is increased, the position of the plot in figure will be higher on the Y axis .The plot will maintain the same general shape. By changing the boiling range of the feed, the shape of the plot can be altered slightly. For example, a heavier feed will result in a percentage increase in C9 and heavier rings to the point where the increase in C9 rings will be in line with the points for C7 and C8.

Carbon number	% increase in ring
-12	-17
16	16
25	25
-21	-21
-30	-30
-39	-39

Butane ratio

When virgin naphtha is charged through a catalytic reformer unit, the mole ratio of i-butane to n-butane in the reactor product is approximately 0.8. Processing cracked naphtha through a reformer results in a slightly higher i-butane/n-butane ratio. This check is extremely useful in identifying problems with reformate sample. If the reformate has been allowed to weather in the laboratory, or if the samples was taken hot, some of the butane will be missing form the sample. Because the concentration of normal butane in reformate is typically four times that of i-butane, more normal butane will be unaccounted for. The result is that the i- butane/n-butane mole ratio will be out of the range 0.8 + 0.15. The i- butane/n- butane ratio for the sample case is 0.7 which is within the acceptable range.

E. Light Ends Ratios

Because the stabilizer overhead are relatively small in comparison to the reformate flow, large errors in these streams will not be identified by the material and hydrogen balances. Comparing light ends ratios is extremely useful in identifying significant errors in light ends ratios rates that may not create a significant deviation in either the material or hydrogen balance. The quantities of methane, ethane, propane, and mixed butanes produced in the catalytic reforming process are approximately equimolar when the light ends (mehtane, ethane, propane, and mixed butanes) is dependent on reactor condition operating conditions, and especially catalyst chloride level (14). For each of the light ends components, a ratio is calculated whereby the moles of each component are divided by the sum of the moles of the light ends components. Table a contain light ends molar yields and resulting ratios calculated from the sample data.

component	Molar yield	Moles/sum of moles
Methane	482.2	0.21
Ethane	552.9	0.24
Propane	627.3	0.27
Mixed butane	638.7	0.28

REFERENCES

1. Petroleum Refining Technology and economics by James H Gary and Glen E .Handwerk.

2. Modeling Commercial Reformers by Lee E Turpin.

3. Meyers, Robert A Handbook of petroleum Refining 3rd Edition.

4. Prasad, Ram; Petroleum Refining technology, 8.3 Catalytic Reforming process, First edition.

5. UOP operating manuals –CCR, Continuous Catalytic Reforming unit.

6. www.wikipedia.com.