

Catalytic Naphtha Reforming: Revisiting its Importance in the Modern Refinery*

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The paper reviews catalytic naphtha reforming, a process that has completed 50 y of existence and has improved the quality of human life globally. Also examines in detail are the historical background of reforming, reaction chemistry, reaction thermodynamics, process details, process variables, commercial processes, and future outlook. Recent environmental regulations have completely re-drawn the objectives of reforming and have even questioned its relevance. Attempts are also made to explain, in brief, the new challenges faced by reforming.

Keywords: Catalytic naphtha reforming, Refinery, Naphtha reforming, Reforming

Introduction

The Charles Stark Draper Prize, often referred to as the Nobel Prize for the engineering profession, has been awarded eight-times since its inception in 1988: for the development of the integrated circuit, the turbojet engine, the FORTRAN computer language, the communication satellite, fibre optics, the creation of the internet, medical drug delivery, and catalytic naphtha reforming. In awarding Vladimir Haensel the Charles Stark Draper Prize in 1997, the National Academy of Engineering gave deserved recognition to catalytic reforming — a revolutionary petroleum refining process that in an environmentally benign way created clean and abundant transportation fuel (Figure 1), enabled the modern plastics industry, and improved standards of living globally¹. Figure 1 shows the quantum jump in oil consumption, explained in part because of reforming, while Figure 2 shows the distribution of the catalysts business amongst various sectors and processes including reforming. Haensel² invented Platforming; the first commercial reforming process licensed by UOP, thereby giving birth to catalytic reforming.

The catalytic reforming process converts petroleum naphtha to high-octane gasoline pool

components. These high-octane gasoline pool components are mainly branched and aromatic hydrocarbons, which are less prone to ignite prematurely in internal combustion engines and thus reduce “knocking” substantially. The naphtha fraction of crude oil, predominantly contains alkanes and cycloalkanes, which in a catalytic reformer are “selectively reformed” to aromatics. Hydrogen an important byproduct of the process, finds numerous applications within the refining industry particularly for the production of clean fuels. The presence of reforming in a refining configuration of the 1980s is depicted in Figure 3.

Hydroforming, the process jointly developed by the Standard Oil Company (now Exxon Research and Engineering Company), the Standard Oil Company of Indiana (now American Oil Company), and the MW Kellogg Company involved the catalytic dehydrogenation of methylcyclohexane (present in petroleum naphtha) to toluene; the concept which eventually led to the development of catalytic reforming. The first commercial unit of Hydroforming went on stream in 1940 at the Pan American Refining Company in Texas City, Texas using a fixed-bed molybdena-alumina catalyst and was carried out at an external hydrogen pressure of about 15 atmos to avoid rapid deactivation of the catalyst.

The second World War played a significant role in catalyzing the technological growth of the petroleum industry and catalytic reforming was no exception. The need for high-octane gasoline for the

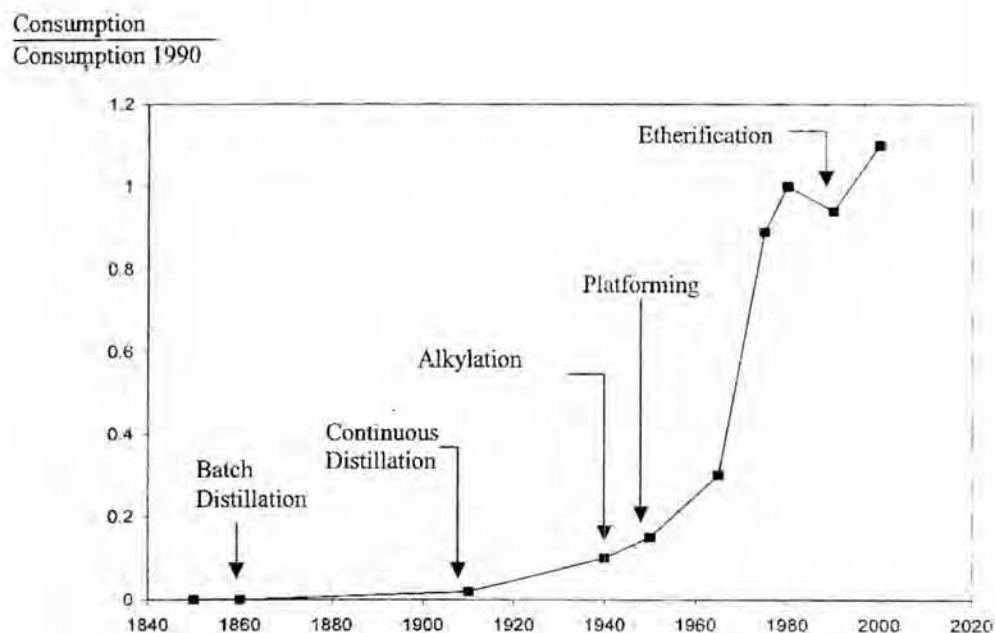
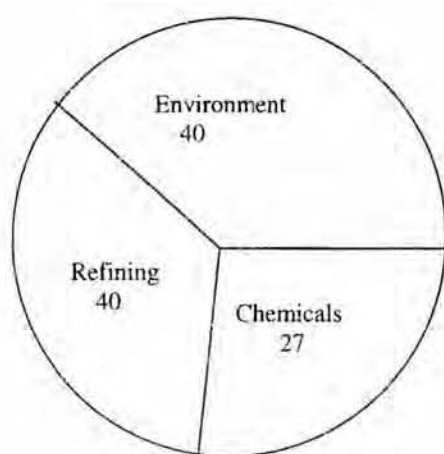
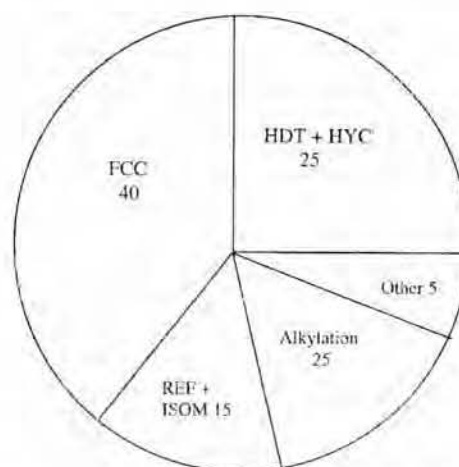
*Dedicated to the memory of Vladimir Haensel

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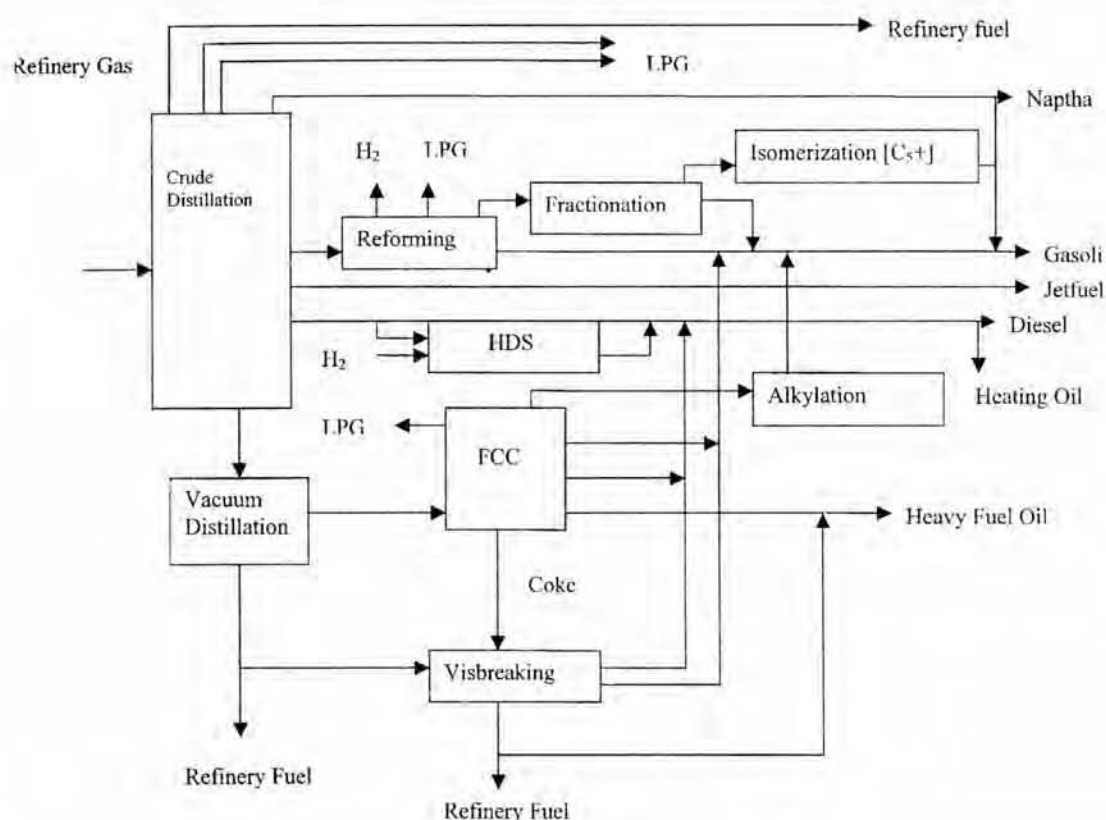
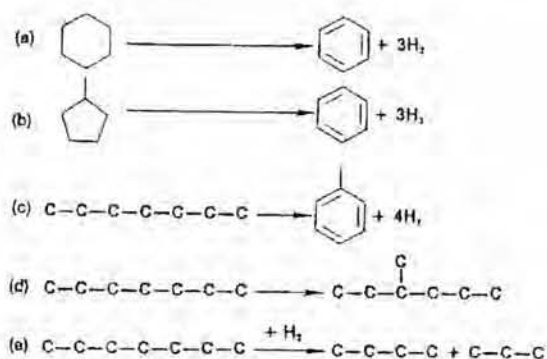
Figure 1 — Oil refining birth through 2000³⁶Figure 2a — Applications of catalysis³⁶Figure 2b — Applications of catalysis in refining³⁶

allied forces was substantial but the need for trinitrotoluene (TNT) obtained from toluene was greater. In those days, TNT was an important, and perhaps the only explosive whose increasing demand resulted in six more units of the Hydroforming process³. UOP developed and licensed the fixed-bed Platforming process using Pt on halided alumina catalyst^{4,5}. It was with Platforming and its vastly superior Pt catalyst that the entire business, science and technology of catalytic reforming achieved iconic status in the refining industry. Almost 50 y later, Platforming as a commercial process of UOP, in

particular, and catalytic reforming, in general, are preferred processes in commercial use the worldover for producing high-octane gasoline, hydrogen, and aromatics as petrochemical feedstocks.

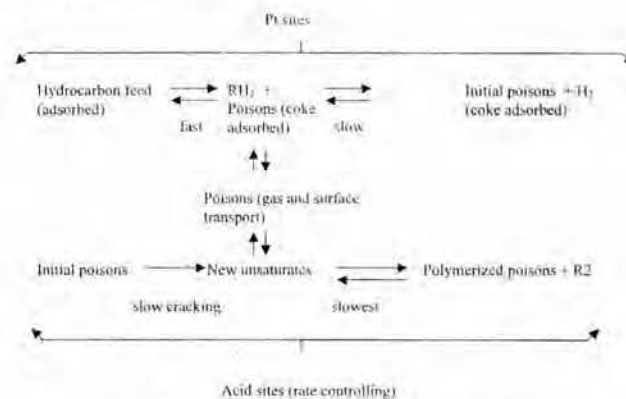
Chemistry of Catalytic Reforming

The important reactions (Figure 4) which occur during catalytic reforming are: (a) Dehydrogenation of naphthenes (cyclohexanes in particular), to aromatics, (b) Dehydroisomerization of alkyl-cyclopentanes to aromatics, (c) Dehydrocyclization of alkanes to aromatics, (d) Isomerization of *n*-alkanes to

Figure 3 — Systematic of a refinery [circa 1980]²⁶Figure 4a — Catalytic reforming reactions⁶

branched alkanes, and (e) Cracking or fragmentation reactions (hydrocracking or hydrogenolysis) yielding products of carbon number lower than that of the reactants⁶.

The dehydrogenation of cyclohexanes (a), the dehydroisomerization of alkylcyclopentanes (b), and the dehydrocyclization of *n*-alkanes (c), to produce aromatics are strongly endothermic reactions and are facilitated by higher temperatures and lower hydrogen

Figure 4b — Postulated mechanism for reforming⁸

partial pressures. The constraint of catalyst deactivation from coke deposition, however, does not allow operation of reforming units at high temperatures and low hydrogen partial pressures dictated by thermodynamics⁷. Paraffin isomerization to alkenes (d) and hydrocracking and hydrogenolysis (e) are exothermic reactions with the latter being hydrogen consuming. Tables 1 and 2 summarize the

thermodynamic and kinetic aspects of the reactions taking place in a commercial reformer.

Mechanistic and Kinetic Features

Reforming catalysts are typically metals supported on an oxide carrier and possess two different types of catalytic activities: an ability to hydrogenate and dehydrogenate hydrocarbons and the ability to catalyze hydrocarbon rearrangements. The former is a purely metal-catalyzed reaction and does not require acid sites, while the latter is catalyzed by acid sites on the support^{8,9}. Dehydroisomerization and isomerization require metal sites for alkane or cycloalkane dehydrogenation to alkenes through a carbocation-like species followed by rearrangement on acid sites to form the isomeric branched alkene and finally yielding the isomeric branched alkane through hydrogenation on metal sites. The transportation of the intermediates between these active sites occurs through the gas phase¹⁰. From the preceding model, we observe that the rates for these reactions are limited by the catalytic activity of the acidic sites. Therefore, continued increase in the metal content in reforming catalysts leads to no appreciable increase in catalytic activity and, in fact, covers up the acid sites and reduces the overall reforming rate⁹.

Reforming Catalysts

Catalysis has played a critical role in the evolution of refining technology (Figure 1) and

catalytic reforming is no exception¹¹. The decisive parameter, which established UOP's Platforming process as the most preferred technology for catalytic reforming was the discovery of the Pt on alumina (Pt/Al₂O₃) catalyst by Haensel².

Chevron³ commercialized the Pt-Re/Al₂O₃ bimetallic catalyst discovered at their research center, changing the course of catalytic reforming and the science of reforming catalysis conclusively. Exxon^{12,13} developed and commercialized the Pt-Ir/Al₂O₃ series of bimetallic reforming catalysts. Both these catalysts were much more active than the traditional Pt catalyst, with the Pt-Ir/Al₂O₃ developed by Exxon displaying substantially greater activity. The bimetallic catalysts all but completely replaced the Pt/Al₂O₃ catalyst in the 1970s and early 1980s. Improved activities of these bimetallic catalysts enabled reforming units to run for longer durations between regenerations, or for a given length of time, allowed lower pressures for higher reformate yields.

Platinum on Alumina

The amount of Pt dispersed on alumina in commercial reforming catalysts is 0.3-0.6 wt per cent. Chlorine is also present in the amounts of 0.3-1.0 wt per cent. These catalysts are prepared by impregnation of alumina with chloroplatinic acid followed by calcination in air between 825-875K. Surface area of the alumina usually used is 150-300 m²/g. The pressure drop and diffusion limitations

Table 1— Thermodynamic data for typical reforming reactions⁶

Reaction	K_p at 500°C, P in atm	ΔH_r , kJ/mol of hydrocarbon
Cyclohexane \leftrightarrow benzene + 3H ₂	6×10^{-5}	220.7
Methylcyclopentane \leftrightarrow cyclohexane	0.086	-15.8
<i>n</i> -hexane \leftrightarrow benzene + 4H ₂	0.78×10^{-5}	265.8
<i>n</i> -hexane \leftrightarrow 2-methylpentane	1.1	-5.9
<i>n</i> -hexane \leftrightarrow 1-hexene + H ₂	0.037	129.6

Table 2 — Rate behavior and heat effects of important reforming reactions⁷

Reaction type	Relative rate	Effect of increase in total pressure	Heat effect
Hydrocracking	Slowest	Increases rate	Quite exothermic
Dehydrocyclization	Slow	Small decrease in rate	Endothermic
Isomerization of paraffins	Rapid	Decreases rate	Mildly exothermic
Naphthene isomerization	Rapid	Decreases rate	Mildly exothermic
Paraffin dehydrogenation	Quite rapid	Decreases conversion	Endothermic
Naphthene dehydrogenation	Very rapid	Decreases conversion	Very endothermic

determine the shape of the reforming catalysts and the preferred shapes are usually pellets or extrudates. Dispersion of the metal on the alumina support is a critical parameter for reforming, as for any catalytic process, and is defined as the ratio of the amount of exposed metal on the surface to the total amount of metal in the catalyst. Chemisorption studies have shown that freshly prepared Pt/Al₂O₃ reforming catalysts are characterized by extremely high Pt dispersion. Hydrogen chemisorption, extended X-ray absorption fine structure (EXAFS) and anomalous X-ray scattering studies have also confirmed high Pt dispersion which exists in an amorphous state, achieves microcrystallinity on reduction with hydrogen. Other studies, e.g., ¹⁹⁵Pt NMR, have also reached similar conclusions⁵.

Acidic Properties of the Alumina

Catalytic reforming as a process stimulated tremendous interest in the role of the support in the science of catalysis and led to some very seminal studies.¹⁴ Alumina, known to be amphoteric, has a lot of hydroxyl groups on its surface which are the prime source for Brønsted (protonic) acidity and responsible for hydrocarbon rearrangement reactions. The presence of chlorine (fluorine, in the early 1950s) in reforming catalysts is thought to impart acidity in alumina by interacting with the surface hydroxyl groups, although fundamental studies and understanding on this particular aspect of reforming catalysts are still not comprehensive⁶.

Platinum-Rhenium Catalysts

These alumina supported bimetallic catalysts generally contain an amount of rhenium comparable to the amount of Pt (often 0.3 wt per cent each). These catalysts are prepared differently from other bimetallic catalysts and organometallic precursors as dirhenium decacarbonyl, Re₂(CO)₁₀ are used to impregnate Pt supported on alumina. Fundamental studies involving characterization techniques as chemisorption, EXAFS and X-ray absorption have shown that rhenium exists in the reduced form and is extremely sensitive to poisoning by sulphur and less sensitive to coke deactivation compared to Pt. It is believed that Pt and rhenium are extensively coordinated to each other in bimetallic clusters, while their individual coordination to oxygen in the alumina framework is small. These studies indicate that the composition and concentration of these clusters vary widely¹⁵.

Platinum-Iridium Catalysts

Platinum-iridium bimetallic clusters are prepared by impregnating the alumina support with an aqueous solution of chloroplatinic and chloroiridic acids¹⁵. After the impregnated support is dried and calcined at mild conditions, it is exposed to flowing hydrogen to reduce Pt and Ir. The catalyst contains comparable amounts of Pt and Ir with a total metal content of 0.5–1.0 wt per cent. The metal dispersion is close to one, implying that almost all Pt and Ir atoms in the catalyst are on the surface. Interaction between Pt and Ir has been studied extensively but conclusive results on the type of interaction, if at all, are still elusive³. Iridium undergoes oxidative agglomeration to form clusters of IrO₂ at high temperatures and so Pt-Ir bimetallic catalysts are calcined at temperatures much lower than those used for Pt on alumina catalysts and logically the regeneration procedures for these catalysts are different.

Platinum-Tin Catalysts

These catalysts were introduced in catalytic reforming units by UOP with their Continuous Catalytic Reforming (CCR) process. The combined Pt and Sn content of these catalysts is less than 0.8 wt per cent. These catalysts are prepared using chlorided precursors and are reduced above 673 K. The Pt-Sn catalysts are the focus of intense research because of two issues: the oxidation numbers of Sn after exposure of the catalysts to hydrogen and the extent to which bimetallic entities of Pt and Sn are present¹⁵. UOP introduced these with the Continuous Catalytic Reformer (CCR) because of the tendency of Pt-Sn/Al₂O₃ to deactivate rapidly.

Platinum/KL Zeolite Catalysts

All commercial catalysts are limited by low selectivity of the aromatization of C₆ and C₇ alkanes relative to that of higher carbon number alkanes in the naphtha boiling range. The yield of these catalysts for converting C₆ alkanes to benzene is typically only about 10 per cent as against 60 per cent for methylcyclopentane and 90 per cent for cyclohexane¹⁶. It has been suggested that this may be due to the acidic chlorided alumina support. A catalyst in which KL zeolite is used as a support for platinum has a significant advantage over conventional reforming catalysts. The KL zeolite has narrow (0.71 nm) unidirectional channels and is not acidic. The Pt in the channels had dispersion almost

equal to one¹⁷⁻¹⁹. The platinum catalyzes aromatization of C₆ and C₇ alkanes with high selectivity. Since the KL zeolite is not acidic, competing reactions of isomerization and hydrocracking are strongly suppressed and thus the aromatization of alkanes proceeds unhindered. This catalyst, however, suffers from extreme sensitivity to sulphur poisoning.

Deactivation and Regeneration

Most catalysts, whether operated commercially or in a laboratory, eventually deactivate. Deactivation is very important in commercial operation because it influences the choice of the operational conditions and fixes the cycle length between regeneration and the total life of the catalyst. Among the processes of petroleum refining and the petrochemical industries, catalytic reforming of naphtha has one of the more complicated deactivation phenomena because the catalyst presents nearly all the known causes of deactivation.

The processing of hydrocarbons is generally accompanied by the formation of carbonaceous deposits on the catalyst surface. The phenomenon is referred to as coking and depends on catalyst composition, operational conditions, and feed composition. Coke is formed on acid catalysts (cracking or isomerization of hydrocarbons), metallic catalysts (methane steam reforming, hydrogenation, or dehydrogenation), and bifunctional metal-acid catalysts (naphtha reforming, paraffin isomerization, or hydrocracking). In the case of naphtha reforming, coke formation is the most rapid cause of deactivation. Reforming catalysts also deactivate because of poisoning by sulphur and nitrogen compounds, sintering (decrease of metallic area), decrease of chloride concentration, and heavy metal deposition.

Bifunctional catalysts coke from accumulation of carbon containing species on the metal and the support⁸. On metallic sites, two models explain coke formation. The first model involves a series of fragmentation and successive dehydrogenation reactions forming carbon atoms, which may combine to form more graphitic and toxic coke deposits. The second mechanism suggests that the routes of coke deposition are based on polymerization reactions with the formation of different types of carbonaceous deposits on the metal surface. Coke formation on acid sites is assumed to arise from polymerization of

dehydrogenated intermediates generated by the metallic function (Figure 4b).

Coke deposition occurs throughout commercial operation on both the acid and metal sites with the rate of deposition being higher at the beginning. It is believed that the initial rapid coke formation occurs mainly on the metal function. Reforming typically contain 0.3 wt per cent Pt which is enough to result in enough steady-state activity to produce all the olefins that can be isomerized or cyclized on the acid function. The initial fast coking of the metal sites until a pseudo steady state of the metal function is reached is called a lineout period. At longer time operations, the acid function is more deactivated by the slow coke deposition.

Commercial naphtha reforming catalysts typically control the main reactions namely the isomerization and dehydrocyclization of C₆-C₉ paraffins, through the acid functionality. However, if the metallic component is less active or the working pressure is very low, the metal may become the controlling function of the main reforming reactions. The length of the run is also important. If the run takes place only during the lineout period, it could be concluded that the metal function controls the catalyst deactivation. Thus, results obtained under certain conditions cannot be extrapolated to other conditions.

The heart of the naphtha reforming process is the catalyst and most of the process improvements have related to catalyst life and stability. Catalyst regeneration includes several steps such as elimination of coke by controlled burning, oxychlorination to revive the metal and acid functionalities, reduction with hydrogen, and, finally activation by sulphating. With respect to catalyst regeneration, there are two models to interpret the coke-burning phenomenon: (i) A homogeneous model, when chemical reaction is the controlling steps of the process. In this case the gaseous reactants diffuse through the solid phase reacting in all the particle volume and (ii) A shrinking core model that proposes the existence of a non-reacting nucleus whose size decreases with time surrounded by a completely burnt shell.

To increase the stability of reforming catalysts, some researchers have evaluated dealuminated ZSM-12, zeolite β , and their composites with γ -Al₂O₃ for the reforming of industrial naphtha. They found that dealuminated ZSM-12 demonstrates unique time-on-

stream stability for the reaction investigated. This behavior is a combined result of the acidity and pore structure of the zeolite which do not favour coke formation. Zeolites with channel intersections slightly larger than the zeolite aperture do not favor coke formation. The results demonstrated that the composite catalysts produce more gasoline-range hydrocarbons and show much better time-on-stream behaviour than conventional $\gamma\text{Al}_2\text{O}_3$ catalysts.

The Reforming Process

Catalytic reforming has evolved rapidly during the past five decades to emerge as one of the most advanced processes available to the refining industry with several commercial licensors (Table 3). The differences characterizing these processes are: (i) Nature of the catalysts used, (ii) Catalyst regeneration procedures, and (iii) Equipment conformation and process configuration. Catalytic reforming processes are modified depending upon process and product configurations which include

higher aromatic conversion, high reformat yields, more efficient catalyst regeneration, longer catalyst life and surface stability, and lower pressures and less hydrogen recycle.

Commercially, reformers are typically operated to produce a product of constant Research Octane Number (RON). Operating conditions of a reformer are usually described in terms of severity. As catalyst deactivation increases, severity is increased to compensate for loss of catalyst activity thereby maintaining product RON. Commercial reformers are designed to process both virgin and cracked naphthas at 5-30 atmos and 700-800K. Pressure is achieved by the partial pressure of hydrogen, which is 50-80 per cent of the total pressure. Hydrogen pressure decreases catalyst deactivation and excessive aromatization. A high RON reformat yield requires lower pressures and more stable catalysts. Industrial catalytic reformers involve three sections: feedstock pretreatment, reaction section, and product separation and stabilizer units.

Table 3 — List of reforming licensors³⁵

Supplier	Catalyst description	Active metal
Acreon catalyst company Procatalyze	AR 403, AR 405: aromatics production	Pt + promoter
	CR201: continuous regeneration	Pt/Sn
	E201-E1000: gasoline/aromatics production	Pt or Pt/Re
	RG series: low to high pressure applications	Pt, Pt/Re, Pt/Re+ promoter
Criterion catalysts company	PHF 4.5: gasoline or BTX production	Pt/Ir + promoter
	PRHF series: gasoline or BTX production	Proprietary
	Kx 120-190 series for gasoline and BTX	
Indian Petrochemical Corporation Limited	IRC 1001, 1002: aromatics and gasoline applications	Pt, Pt/Re
Instituto Mexicana del Petroleo	MP-RNA-1, 2: gasoline/BTX	Pt/Re
	IMP-RNA-4: for continuous processes	Pt/Sn
UOP	R-30 series: continuous regeneration	Proprietary
	R-50 series: high severity semi-regeneration	Pt/Re
	R-60 series: higher stability	Pt/Re
	R-72 series: higher severity semi-regeneration	Proprietary
	R-132, 134 series: continuous regeneration	Proprietary
Katalena GmbH	8815/03, 05: mono metallic [all series for gasoline/BTX]	Pt
	8819/B: bimetallic	Pt/Re
	8823: bimetallic	Pt/Re
	8842: continuous regeneration	Pt/Sn

Feedstock Pretreatment

The prime objective of feedstock pretreatment is removal of permanent catalyst poisons such as arsenic, lead, and copper and to reduce temporary catalyst poisons such as, sulphur, oxygen, and nitrogen to lower levels (Table 4). Naphtha hydrotreatment involves vapor-phase reaction with hydrogen over a sulphur-resistant catalyst such as, Co-Mo/Al₂O₃, followed by cooling, phase separation, and efficient stripping of all H₂S and NH₃ out of treated naphtha. Water is also removed as its presence leads to acidic modification of alumina. Chlorine, at a predetermined level in the catalyst, is necessary to influence and generate desired alumina acidity but chlorine in the feed leads to selectivity shifts in the catalyst, and frequently, excessive hydrocracking. Chlorine is thus washed away from the feed using water or alcohol.

The Reforming Reactor

The reaction section of a conventional reformer consists of multi-bed reactors in series with pre- and re-heaters between the reactors. Desired product RON requires at least three or four reactors. The feedstock, naphtha, is mixed with hydrogen (usually recycled

from the process itself) and heated to the desired temperature before it enters the first reactor. Temperature profiles are an important consideration in reactor design (Table 5). The overall reforming reactions are endothermic and isothermal operation, although desirable, is impractical on a commercial scale. To overcome this difficulty, the reactors are separated into several adiabatic zones operating at 755K with heaters in between stages to supply necessary heat of reaction, thereby holding the overall series of reactors at a constant temperature.

Reactor systems are selected depending on reforming unit configurations. Initially, axial downflow reactor systems were used as they were cheaper but the huge pressure drops created by them led to the usage of radial downflow reactors in fixed-bed systems. Presently, many reforming units use a combination of both types of reactors. The reaction temperature in the first reactor decreases rapidly due to the dehydrogenation of cycloalkanes to aromatics, which consumes heat. The effluent from the first reactor is then heated and fed to the second reactor where it undergoes dehydroisomerization of cyclopentanes at a slower rate than in the first reactor. The second reactor operates with a temperature drop of 295-305K. The last stage reactor involves hydrocracking and hydrogenolysis, which is exothermic leading to slight temperature changes. The first reactor is the smallest in size followed by the second, while the third and fourth are very large reactors reflecting the time taken by the reactions

Table 4 — Naphtha Pretreatment Indicators²⁴

S ≤ 10 ppm or 5 ppm at high severity	N ≤ 1 ppm
H ₂ O ≤ 4 ppm	Pb + As + Cu < 20 ppb

Table 5 — Typical operating conditions for a three-reactor system^b

	Reactor 1	Reactor 2	Reactor 3
Inlet temperature, K	775	775	775
Exit temperature, K	706	844	769
Temperature drop, K	69	31	6
Octane number	65.5	79.5	90.0
Octane-number increase	27.0	14.0	10.5
Principal reactions	Dehydrogenation, Dehydroisomerization	Dehydrogenation, Dehydroisomerization, Hydrocracking, Dehydrocyclization	Hydrocracking, Dehydrocyclization
LHSV, h ⁻¹ per reactor	5.5	2.4	1.7
Per cent of total catalyst charge	15	35	50

taking place in each of these reactors. The catalyst loaded in the first reactor is only 10-20 per cent of the total catalyst charge. Temperature profile (ΔT) along the reactors is another important parameter and is indicative of the type of reactions occurring in each reactor.

Product Separation and Stabilization

Effluents from the reactors are cooled and separated into gaseous and liquid products. The gaseous products consist of 60-90 mol per cent hydrogen and the rest C_{1-4} hydrocarbons. The liquid product, known as the reformate, consists of C_{5-10} hydrocarbons with aromatics in the range of 60-70 wt per cent. The crude reformate is purified in a stabilizer where volatile and light hydrocarbons are removed, using a single-column operation under sufficient pressure to permit condensation of reflux from the overhead vapor. Part or most of the overheads are removed as vapor.

Process Classification

Catalytic reforming processes are classified, based on the mode and frequency of catalyst regeneration, into three types: (a) Semi-regenerative, (b) Cyclic (Fully regenerative), and (c) Continuous Regenerative (Moving bed) process. There are more than 800 commercial (Table 6) installations of the catalytic reforming processes worldwide with a total capacity of 9.5 million barrels/d²²⁻²⁴.

Semi-regenerative Process

The semi-regenerative catalytic reforming process is characterized by continuous operation over long periods with decreasing catalyst activity and increasing reforming severity to maintain conversion to a specific RON. The semi-regenerative process is the conventional reforming process, which operates continuously for more than 1 y. Eventually the reformers are shut down periodically and the catalyst

beds are regenerated at low pressure of about 8 atmos with air as the source of oxygen. The catalyst inventory can be regenerated 5-10- times before its activity falls below the economic minimum, when it is replaced. As catalytic activity decreases, aromatic yield and hydrogen purity also drops because of increased hydrocracking.

The advent of bi- and multi-metallic catalysts allowed the operation of semi-regenerative units at 14-17 atmos for the same cycle lengths compared to higher pressures of 30 atmos using Pt. Semi-regenerative reformers are generally built with three to four catalyst beds in series (Figure 5). The fourth reactor is usually added to some units to allow an increase in either severity or throughput while maintaining the same cycle length. Catalyst amount increases with the cycle length. The product RON achievable through this is usually 85-100, depending on optimized feedstock quality, gasoline qualities and quantities, and operating conditions required to achieve a specified cycle length. Most licensors have semi-regenerative design options (Table 3).

Cyclic (Fully Regenerative) Process

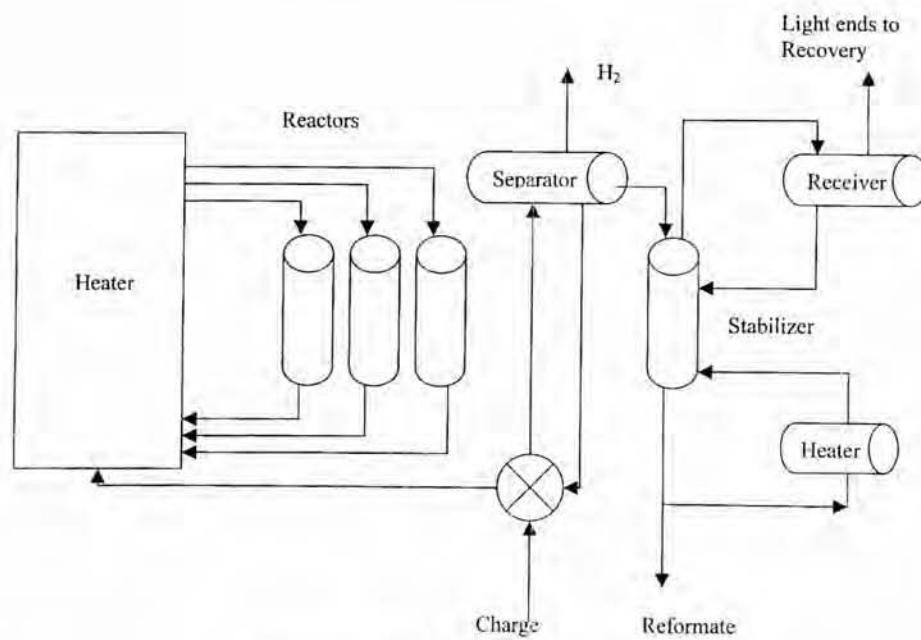
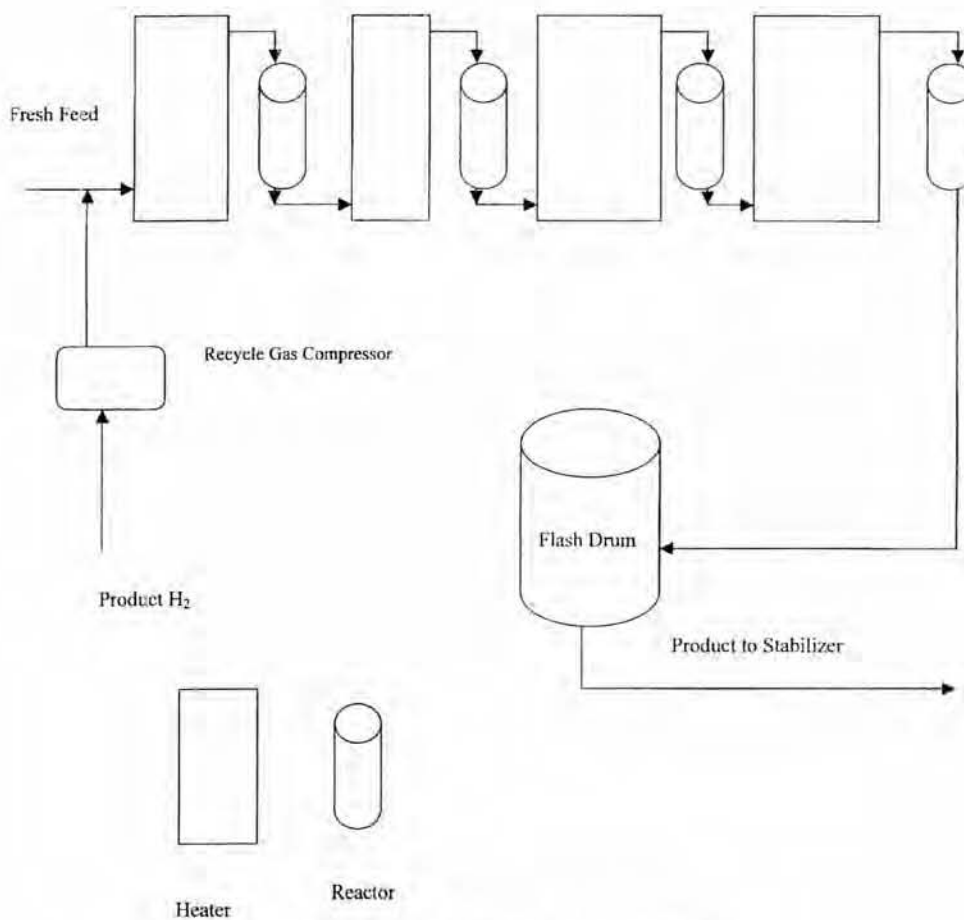
The cyclic process, typically uses a train of five to six fixed catalyst beds, similar to the semi-regenerative process, with one additional swing reactor, which is a spare reactor used to substitute any of the regular reactors in the train while the regular reactor is being regenerated (Figure 6). This enables only one reactor to be taken off-stream while the whole process and reformate yields continue unaffected. Catalyst regeneration takes place at longer intervals as compared to the semi-regenerative process. The cyclic reformer operates at low pressure, wide-range boiling feed and low hydrogen to hydrocarbon ratio.

The cyclic process produces reformate of RON 100-104 but also leads to extensive coking due to low

Table 6 — Regional distribution of catalytic reformers by process design in 1993²⁴

Region	Per cent of Reformers			
	Semi-regenerative	Cyclic	Continuous	Other ^a
United States	57	13	14	16
Europe	66	11	17	6
Japan	70	10	15	5

^a Other includes non-regenerative and moving bed systems

Figure 5 — Semi-regenerative reformers³⁵Figure 6 — Cyclic regenerative reformers³⁵

pressure and high-octane severity. Using lower pressures enables production of a higher C_{5+} reformat yield and hydrogen. The process suffers from the drawbacks that the reactor sizes should all be the same to enable switching and also that the reactors alternate between a reducing atmosphere during normal operation and an oxidizing atmosphere during regeneration.

Continuous Regenerative (Moving Bed) Process

UOP in the late 1960s made another advance in the technology of catalytic reforming by introducing the Continuous Catalytic Reformer (CCR) which produces high octane reformat and high-purity hydrogen on a continuous basis, using small amounts of a highly active catalyst. The process has the best of the cyclic reforming process while at the same time avoiding its drawbacks. In this process, small quantities of catalyst are continuously withdrawn from an operating reactor, transported to a regeneration unit, regenerated and then returned to the reactor system. The most common design involves stacking of all reactors on top of one another with the last reactor set beside the stacked reactors. The reactor system has a common catalyst bed that moves as a column of particles from the top to bottom of the reactor. Operating pressures are in the range of 3.5-17 atmos to produce a reformat of RON 95-108 (Figure 7).

Operating Parameters

Catalytic reformers are designed for flexibility in operation and product configuration for which

changes in unit operating conditions are carried out by changes in operating parameters (Table 7 and 8). The variables, which affect performance of the catalyst and change the yield and quality of reformat are feedstock properties, reaction temperature, space velocity, reaction pressure, and hydrogen-to-hydrocarbon mole ratio.

Feedstock Properties

Boiling range of the feed is an important parameter which can be controlled and the maximum ASTM end point of 478K is specified for reformer reactor charge. This is because hydrocarbons boiling above 478K are known to form polycyclic aromatics and thus coke. As a rule, a change in temperature by 13K in feed ASTM end point costs about 35 per cent of catalyst life between ASTM end point ranges of 463-491K for the feed. Straight run naphthas are the major feedstocks for reformers²⁵.

Feedstocks with appreciable content of unsaturated hydrocarbons arising from thermally cracked, catalytically cracked, coker and pyrolysis naphtha must all be hydrotreated before reforming to prevent undue hydrogen consumption and excessive catalyst deactivation. In addition to having sulphur and nitrogen, these stocks also contain substantial olefins and diolefins, which are undesirable in reformer feed for several reasons. The most important side reaction in a reformer is hydrogenation of olefins causing excessive hydrogen consumption. In addition, this undesired side reaction markedly reduces the reformat RON. More importantly, olefins tend to polymerize and form coke on catalyst surfaces.

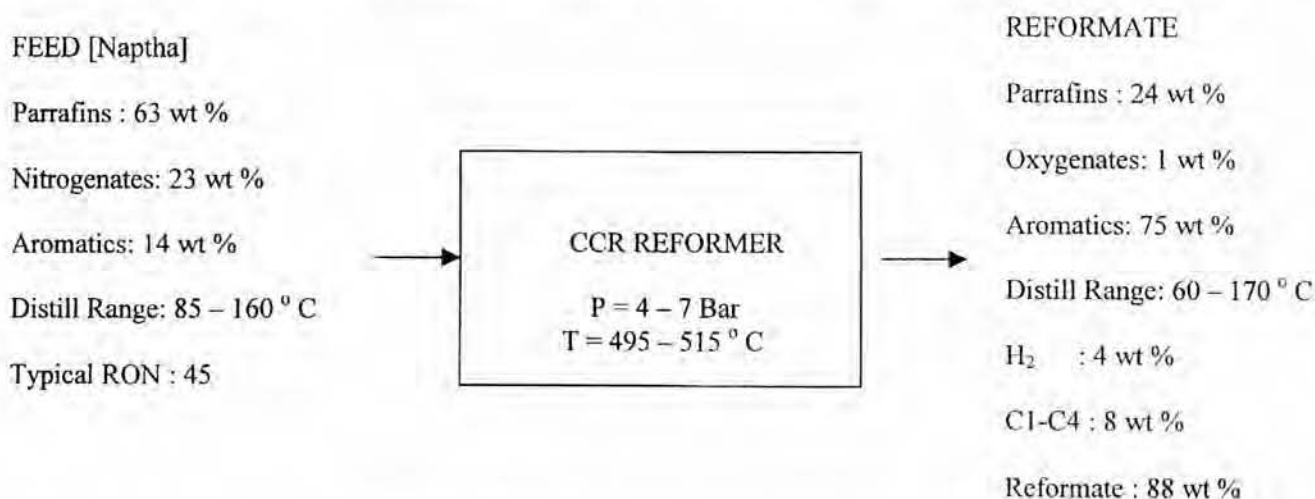


Figure 7 — Mass balance for continuous catalytic reforming¹⁵

Table 7 — Yield-octane relationship, reforming C₆ 633K naphtha, constant temperature²³

Pressure (atmos)	C ₅₊ yield (vol., per cent)	Octane C ₅₊ (R+O) ^a
7	90	92
7	83	99
14	87	92
14	80	99
17	82	92
17	76	99
34	88	92

^a Research octane number in the absence of tetraethyl lead.Table 8 — Influence of feed properties and product distribution²⁴

	H ₂ purity ^a	H ₂ yield	C ₅ ⁺ yield	Delta temp.	Reactor temp.
Feed property					
API	-	-	-	-	+
Paraffins	-	-	-	-	+
Naphthenes	+	+	+	+	-
Aromatics	-	-	+	-	0
Initial boiling point	-	-	-	-	-
Final boiling point	0(-)	+	+	+	+
Process variable					
Separator pressure	+	0	+	0	0
Separator temperature	-	0	-	0	0
Reactor pressure	-	-	-	-	-
Reformat RONC	-	+	+	+	+

^a +, Increase; -, Decrease; 0, No effect

Reaction Temperature

Reformers are generally designed as a series of reactors, which lead to changes in catalyst bed temperatures as feed flows through them. It is thus common practice to measure either the Weighted-Average reactor Inlet Temperature (WAIT) or the Weighted-Average Bed Temperature (WABT). WAIT is the sum of the inlet temperature to each reactor multiplied by the weight per cent of total catalyst in each reactor. Similarly, WABT is the sum of the average of the inlet and outlet temperatures of each reactor multiplied by the weight per cent of the catalyst in the reactor. In day-to-day operations, it is always easier to operate WAIT than WABT.

Reaction temperatures are chosen to balance increased catalyst activity (maximum in the range 733-798K) with increased deactivation rate (occurring in the temperature range 755-773K). Low-pressure processes are operated at slightly higher temperatures to optimize conversions to high-RON products. Catalytic reforming results in increased reformat RON with reactor temperature and as a rule for the RON range of 90-95, WAIT should increase by 2-3K/RON increase²⁶. For a RON range of 95-100, WAIT increase should correspond to 3-4K/RON increase. Each feedstock, however, has its own temperature-octane relationship and there is no widely accepted correlation to account for all feedstock-

temperature relationships. Also, increased RON reformates have a reduction in yield by about 13 volume per cent of the reformer charge.

Space Velocity

Space velocity is an important reforming process variable and is a measure of the contact time between the reactants and the catalyst. This is expressed as either the Liquid Hourly Space Velocity (volume per hour of reactor charge per volume of catalyst, LHSV) or the Weight Hourly Space Velocity (weight per hour of reactor charge per weight of catalyst, WHSV). Modern commercial reformers usually operate in an LHSV range of 1-2/h. At lower LHSV values, contact time increases, leading to undesired side reactions and increased hydrocracking, reducing reformat yield. This choice, however, represents a compromise between reducing undesired hydrocracking and increase in desired dehydrocyclization. Aromatization and isomerization, however, are not affected by changes in space velocity as these reactions are very fast and approach equilibrium values even at lower contact times.

Generally, for a reformat of 90-100 RON, doubling LHSV requires an increase of 15-20K in reactor inlet temperature. Higher paraffinic naphthas require a 20-30K increase in reactor inlet temperature as space velocity doubles. Naphthas, which are low in paraffins, require only 8-12K increase in reactor inlet temperature as space velocity doubles²⁷.

Reaction Pressure

Over the past five decades, reformer unit pressures have dropped substantially. Reformers of the 1950s used a pressure range of 19-35 atmos while modern reformers operate between 5-11 atmos. Each of the three or four reformer reactors has different pressures and an average reactor pressure is preferred. Decreased pressures lead to increased aromatics and hydrogen yields but also increase coking and catalyst deactivation. It has been demonstrated that at 100 RON, there is an increase in the per cent yield of reformat from 79.7 to 83.5 by a reduction in pressure from 21 to 8 atmos. In other words, at the 100 RON level, liquid yield increases or decreases by about 2 vol per cent of charge/ 8 atmos change in pressure. At the 90 RON level, the yield difference is about 1 liquid vol per cent of charge/8 atmos change in pressure^{28,29}. Similar quantitative correlations have not yet been reported for hydrogen yield.

Hydrogen-to-Hydrocarbon Ratio

Hydrogen is essential in reforming to avoid unwanted side reactions and reduce catalyst deactivation. High hydrogen-to-hydrocarbon ratios require high hydrogen recycle rates and increased energy costs. Operating at reduced hydrogen-to-hydrocarbon ratios leads to savings in terms of energy costs and hence the value chosen is lower bound by the desired amount of hydrocracking and the maximum acceptable deactivation. Reformers designed in the 1950s used a hydrogen-to-hydrocarbon ratio of 8-10 and a hydrogen partial pressure of 19-35 atmos while modern reformers operate in hydrogen-to-hydrocarbon ratio range of 2-5 and a partial hydrogen pressure of 5-11 atmos, a change due to highly active catalysts.

Recent Developments

Catalytic reforming, in addition to fulfilling its original objective of producing high octane gasoline has also been used for various applications, including production of aromatics, liquefied petroleum gas (LPG), hydrogen, and upgrading olefinic feedstocks and raffinates. Almost 75 different reforming catalysts are available currently for specific goals, using specific feedstocks. Catalytic reforming is presently used for three broad purposes: octane boosting, aromatics production and olefinic feedstock upgrading. Recent developments have focused on imparting flexibility to reforming units to process variable feedstocks using new catalysts.

Octane Boosting

This is a post-reforming process which cracks straight chain paraffins selectively using a metal (Ni) impregnated in a small pore zeolite (ZSM-5 or Erionite) at 25 atmos pressure, hydrogen-to-hydrocarbon ratio of 7 and temperatures around 600K. Commercial licensors of similar processes include ExxonMobil (Mforming) and UOP (Selectoforming).

Aromatics Production and Olefinic Feedstock Upgrading

Catalytic reformers with these objectives process very narrow feed cuts in the range of 333-363K for benzene production and 383-413K for toluene and xylene production with the exact cut points depending on crude source. Gasoline production requires full range naphtha. These reformers operate at high severity to maximize aromatics production. Some of

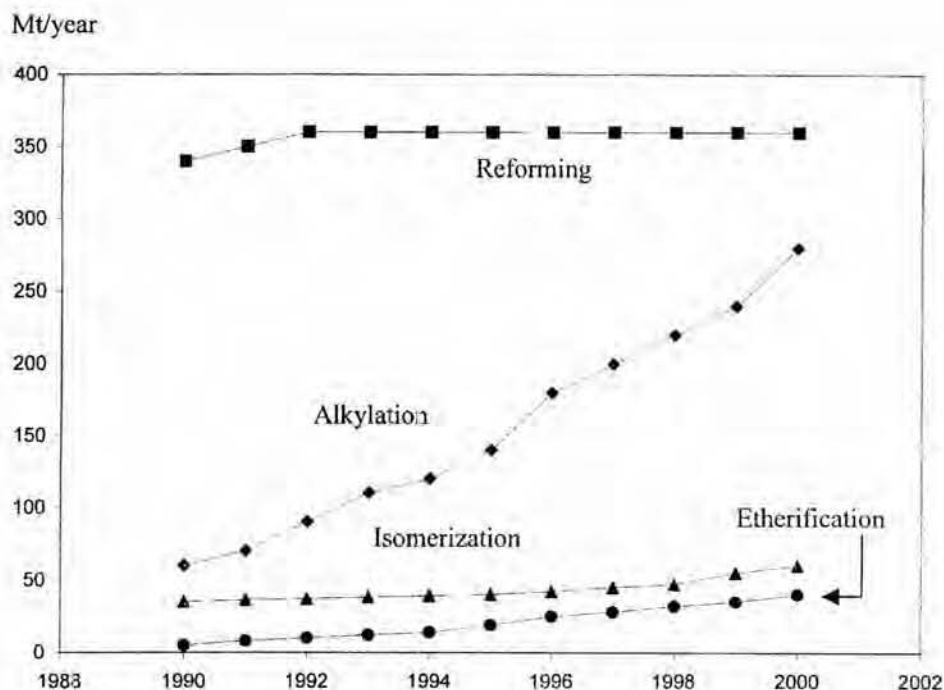


Figure 8 — Oil refining birth through 2000(ref.36)

the well-known processes available towards these objectives include M2Forming (from ExxonMobil) which processes olefinic feedstocks and thermally cracked naphtha at low pressures and high temperatures, Aroforming (from Salutec, Australia and IFP, France) using a Ga impregnated ZSM-5 catalyst to convert LPG and light naphtha to aromatics (with no hydrogen recycle), and the BP-UOP Cyclar process, quite similar to Aroforming. The Cyclar process has had some success in the past but has not been very popular of late³⁰.

Beyond Environmental Regulations

The Clean Air Act Amendments of 1990 impacted catalytic reforming by laying restrictions on fuel quality to improve emission standards. Limits on benzene to a 1 volume per cent maximum and reduced Reid Vapor Pressure (RVP) have forced a complete rethink of the process and is the biggest challenge facing reforming. The offset in octane number caused by reduction in benzene was to be met by the addition of oxygenates such as methyl *tert*-butyl ether (MTBE) which has a RON of 117. This has, however, received a major setback with the recent decisions to stop using MTBE as an octane-enhancing additive because of its groundwater polluting potential.

With these developments, there is a reduced emphasis on the use of benzene for octane enhancement and development of catalysts and technologies which alkylate benzene and toluene to xylenes and C_9 aromatics would be the new challenges for the refining industry. Existing reforming catalysts have to be modified or new post-reforming processes added or discovered, to meet this challenge. This would also lead to reluctance in processing full range naphtha to avoid benzene production. For octane number enhancement, the thrust shall be on catalysts and technologies that isomerize the lighter C_6 and C_7 paraffins to branched isomers with higher RON.

RVP constraints will result in eliminating butane from gasoline: excess butane being available for conversion into *iso*-butane and *iso*-butylene, which, in particular, is an important feedstock for synthesis of MTBE. This is particularly important in countries like, India and China, which have to cope up with the Clean Air Act and are still using MTBE but face an acute shortage of *iso*-butylene as its feedstock.

Petrochemical capacities are on the rise globally and especially in the Asia-Pacific where the per capita consumption of petrochemical products is less than European and the US values by an order of

magnitude^{31-34,37}. Considering the above scenario for the petrochemical industry and the product pattern involving LPG³⁰, it is expected that major reforming units would now be built in the Asia-Pacific³⁷, which not only require aromatics, but also huge amounts of LPG. It would be ideal if reformers could produce only aromatics and hydrogen but this is an unlikely scenario in the near future and so the preferred product distribution would be aromatics and LPG. Thus, on an overall basis, catalytic reforming is expected to increase slightly or plateau out (Figure 8) for octane enhancement objectives but has a strong outlook as far as aromatics production is concerned^{34,37}.

Conclusions

Benzene, toluene, and xylene are critical feedstocks for the petrochemical industry and we expect that they will be available to a large extent from reforming units. We feel that there will be renewed focus on reforming as a process towards production of aromatics and hydrogen. Catalytic reforming is by far the most effective producer of hydrogen whose most efficient use is for producing clean fuels in the refinery and thus, hydrogen consumption is expected to be very strong for quite some time in the future. Higher hydrogen production means operations of reformers at lower pressures and many reforming licensors have processes available to meet this requirement.

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References

- Internet, web site of the National Academy of Engineering, www.nae.edu.
- Vladimir Haensel, *Heterogeneous catalysis — Selected american histories*, edited by B H Davis and W P Hettinger (Jr), 222 (ACS Symposium Series, Washington DC) 1983.
- Sinfelt J H, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger and J Weitkamp (VCH, Weinheim) 1997.
- Heinemann H, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger and J Weitkamp (VCH, Weinheim) 1997.
- Peer R L, Bennett RW & Felch D E, UOP Platforming leading octane technology into the 1990's, *Catal Today*, **18** (1994) 473.
- Sinfelt J H, *Bimetallic catalysts: Discoveries, concepts, and applications* (Wiley, New York) 1983.
- Bourmonville Jean-Paul & Franck Jean-Pierre, *Hydrogen effects in catalysis*, edited by Z Paal and P G Menon, (Marcel Dekker, New York) 1988.
- Gates B C, Katzer J R & Schuit G C A, *Chemistry of catalytic processes* (McGraw Hill, New York) 1979.
- Sinfelt J H, Bifunctional catalysis, *Adv Chem Eng*, **5** (1964) 37.
- Weisz P B & Swegler E W, Stepwise reaction on different catalytic centers: isomerization of saturated hydrocarbons, *Science*, **126** (1957) 31.
- Martino G, Courty P & Marcilly G, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger, and J Weitkamp (VCH, Weinheim) 1997.
- Sinfelt J H, Polymetallic cluster compositions useful as hydrocarbon conversion catalysts, *US Pat*, 3953368, 1976.
- Sinfelt J H, Combination reforming, *US Pat*, 3791961, 1974.
- Bond G C, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger and J Weitkamp (VCH, Weinheim) 1997.
- Boitiaux J P, Devès J M, Didillon B & Marcilly C R, *Catalytic naphtha reforming: Science and technology*, edited by G J Antos, A M Aitani and J M Parera (Marcel Dekker, New York) 1995.
- O'Connor C T, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger and J Weitkamp (VCH, Weinheim) 1997.
- Corma A, Transformation of hydrocarbons on zeolite catalysts, *Catal Lett*, **3** (1993) 22.
- Derouane E C & Vanderveken D J, Structural recognition and preorganization in zeolite catalysis: direct aromatization of hexane on zeolite-L based catalysts, *Appl Catal*, **45** (1988) L15.
- Larsen G & Haller G L, Metal-support effects in platinum/L-zeolite catalysts, *Catal Lett*, **4** (1990) 375.
- Prasada Rao T S R, *C K Murthy memorial lecture*, Indian Institute of Chemical Engineering, Hyderabad, 1991.
- Creyghton E J & Downing R S, Shape-selective hydrogenation and hydrogen transfer reactions over zeolite catalysts, *J Mol Catal A: Chem*, **134** (1998) 47.
- Sinfelt J H, Bimetallic catalysts, *Sci Am*, **253**, 3 (1985) 90.
- Fung S C, Regenerating a reforming catalyst, *Chemtech*, (January 1994) 40.
- Aitani A M, *Catalytic naphtha reforming: Science and technology*, edited by G J Antos, A M Aitani and J M Parera (Marcel Dekker, New York) 1995.
- Le Page J P, *Applied heterogeneous catalysis* (IFP Publications, eds Technip, Paris) 1987.

- 26 Prins R, *Chemistry and chemical engineering of catalytic processes*, edited by R Prins and G C A Schuit (Sijthoff and Noordhoff, Alphen aan den Rijn) 1980.
- 27 Peer R, Bennet R & Bakas S, *Oil Gas J*, (May 30, 1988).
- 28 Rhodes A K, *Oil Gas J*, (October 11, 1993).
- 29 Little D M, *Catal Reform* (Peawell, Tulsa) 1985.
- 30 Sivasanker S & Ratnasamy P, *Catalytic naphtha reforming: Science and technology*, edited by G J Antos, A M Aitani and J M Parera (Marcel Dekker, New York) 1995.
- 31 Takeda M & Tamura K, China's petrochemical industry, *Chemtech*, (January 1996) 42.
- 32 Takeda M & Tamura K, India's petrochemical industry, *Chemtech*, (July 1997) 50.
- 33 Morse P M., Petrochemicals: Dark skies and beyond, *Chem Eng News*, (March 23, 1998) 17.
- 34 *Oil Gas J*, (October 12, 1998).
- 35 Magee John & Dolbear Geoffrey, *Petroleum catalysis in nontechnical language* (PennWell Publishing Company, Tulsa) 1998..
- 36 Martino G, Courty P & Marcilly C, *Handbook of heterogeneous catalysis*, edited by G Ertl, H Knözinger and J Weitkamp (VCH, Weinheim) 1997.
- 37 Tullo A H, The next wave, *Chem Eng News*, (June 2, 2003) 26.