Platforming in Petroleum Refining: A Comprehensive Technical Review

1. Introduction to Platforming

1.1. Definition and Significance in Modern Petroleum Refineries

Platforming is a catalytic reforming process extensively employed within the petroleum refining industry. Its fundamental purpose is the chemical transformation of low-octane naphthas—a complex mixture of hydrocarbons derived from crude oil distillation—into high-octane reformate. This reformate serves as a critical blending component for the production of high-quality gasoline and is also a primary source of aromatic hydrocarbons. The process is pivotal for enhancing the quality of motor fuels and for generating valuable chemical intermediates, making it indispensable in modern refinery operations. Indeed, catalytic reforming, of which Platforming is a prominent variant, is considered one of the most important processes in oil refineries for producing high-octane gasoline, with the vast majority of gasoline produced worldwide being derived from it.

The significance of platforming extends beyond simple octane enhancement; it acts as a cornerstone for integrating refining and petrochemical operations. This integration is possible due to its dual output of high-octane gasoline components and valuable aromatic compounds, primarily benzene, toluene, and xylenes (BTX), which are fundamental feedstocks for the petrochemical industry. This dual capability means that platforming units are not solely focused on fuel production but are also pivotal for refineries aiming to diversify into or expand their petrochemical output. Such diversification is a key strategic trend in the contemporary refining industry, driven by fluctuating fuel demands and the growing market for chemical products. Consequently, investment decisions and operational strategies for platforming units are intricately linked to the dynamics of both the fuels market (octane demand) and the petrochemicals market (BTX value).

The historical trajectory of reforming technology, from its initial concepts to the advanced platforming processes used today, reflects a continuous pursuit of enhanced efficiency, improved product quality, and greater operational flexibility. The first commercial catalytic reforming process using a platinum catalyst was developed by Universal Oil Products (UOP) in 1949, marking a significant milestone. Early reforming units were often non-regenerative, meaning the catalyst, once deactivated, had to be replaced rather than regenerated in situ. The subsequent evolution through semi-regenerative, cyclic, and ultimately continuous catalyst regeneration (CCR) technologies signifies substantial technological advancements. These developments were driven by the need to improve catalyst longevity, maximize on-stream factors, and enhance product yields, largely in response to the demands of evolving automotive engine technologies (requiring higher octane fuels) and increasingly stringent environmental fuel specifications.

1.2. Primary Objectives: High-Octane Gasoline, Aromatic Hydrocarbons (BTX), and Hydrogen Production

The primary objectives of the platforming process are threefold: the production of high-octane gasoline (reformate), the generation of aromatic hydrocarbons (specifically BTX), and the co-production of hydrogen. Low-octane naphtha, typically derived from the atmospheric distillation of crude oil, is catalytically converted into reformate, which is a high-octane blending stock essential for formulating modern gasolines. Simultaneously, the process yields significant quantities of aromatic hydrocarbons, particularly benzene, toluene, and xylenes (BTX), which are vital feedstocks for the petrochemical industry, used in the manufacture of plastics, synthetic fibers, and various other chemical products.

A crucial co-product of the platforming process is hydrogen. This hydrogen is not merely a byproduct but a valuable commodity within the refinery. It is extensively utilized in other essential refinery processes, most notably hydrotreating and hydrocracking units. Hydrotreating processes employ hydrogen to remove sulfur, nitrogen, and other impurities from various refinery streams, enabling the production of cleaner fuels that meet stringent environmental regulations. Hydrocracking units use hydrogen to convert heavy hydrocarbon fractions into lighter, more valuable products such as gasoline, diesel, and jet fuel.

The co-production of hydrogen provides a critical economic and operational advantage to the platforming process, making it integral to the overall hydrogen management strategy of a refinery. As environmental regulations worldwide become increasingly stringent, particularly concerning the sulfur content in transportation fuels, the demand for hydrotreating, and consequently for hydrogen, has risen significantly. The platformer's role as a major internal source of relatively high-purity hydrogen enhances its value proposition beyond just octane and aromatics production. It becomes a key enabler for the refinery to process more challenging (e.g., higher sulfur) crude oils and to produce a slate of environmentally compliant fuels. The efficiency of hydrogen production in the platforming unit can, therefore, directly influence the refinery's overall processing flexibility and its capacity to meet market demands for clean fuels.

Furthermore, the platforming process offers considerable operational flexibility. By adjusting feedstock selection (e.g., C6-C8 naphtha cuts are preferred for maximizing BTX production, while C7-C9 cuts are often favored for high-octane gasoline components) and operating severity (e.g., temperature, pressure, space velocity), refiners can shift the product slate to preferentially maximize either high-octane gasoline for the motor fuel pool or specific aromatic compounds for the petrochemical market. This adaptability allows refineries to respond to fluctuations in market demand and pricing for different products, thereby optimizing profitability. The increasing global trend towards greater integration between refining and petrochemical operations further underscores the strategic importance of this flexibility , positioning the platforming unit as a pivotal link between fuel production and chemical manufacturing.

2. Fundamental Chemistry of the Platforming Process

The platforming process achieves the transformation of low-octane naphtha into high-value products through a complex series of chemical reactions occurring simultaneously over a bifunctional catalyst. These reactions primarily involve the rearrangement and restructuring of hydrocarbon molecules.

2.1. Key Chemical Reactions and Mechanisms

The principal chemical transformations occurring during platforming include the dehydrogenation of naphthenes to aromatics, the dehydrocyclization of paraffins to aromatics, the isomerization of both paraffins and naphthenes, and, to a lesser extent, the hydrocracking of paraffins. These reactions are catalyzed by bifunctional catalysts possessing both metal and acid sites.

The desired reactions, namely aromatization (dehydrogenation of naphthenes and dehydrocyclization of paraffins) and isomerization, primarily aim to increase the molecular complexity (e.g., formation of cyclic and aromatic structures) and branching of the hydrocarbon molecules. These structural changes directly correlate with an increase in the octane number of the gasoline pool. For instance, aromatics possess very high octane numbers, and branched paraffins (isoparaffins) have significantly higher octane ratings than their linear counterparts. Undesired reactions, such as excessive hydrocracking, lead to the formation of lighter products (LPG and fuel gas), reducing the liquid yield of valuable gasoline-range reformate. However, a controlled degree of hydrocracking can be beneficial in converting very low-octane normal paraffins.

Hydrogen plays a multifaceted role in the platforming process. It is a significant product of the primary octane-enhancing reactions (dehydrogenation of naphthenes and dehydrocyclization of paraffins). Conversely, it is consumed during hydrocracking reactions. Platforming units are designed to be net producers of hydrogen, a feature critical for refinery hydrogen balance. The yield of hydrogen is, however, sensitive to the operating severity and the composition of the feedstock. Higher severity operations, which may favor increased hydrocracking, can potentially reduce the net hydrogen yield. Similarly, feedstocks richer in naphthenes tend to produce more hydrogen. This interplay necessitates careful optimization of operating conditions and catalyst selection to meet targets for both octane improvement and hydrogen production.

2.1.1. Dehydrogenation of Naphthenes to Aromatics

This is one of the most important and desired reactions in platforming, responsible for a significant portion of the octane uplift and hydrogen production. It involves the conversion of naphthenes (saturated cyclic hydrocarbons like cyclohexane and its derivatives) into their corresponding aromatic hydrocarbons (e.g., benzene, toluene, xylenes) with the concurrent release of hydrogen molecules. An example is the conversion of methylcyclohexane to toluene. $C_7H_{14} \text{ (methylcyclohexane)} \rightarrow C_7H_8 \text{ (toluene)} + 3H_2$ This reaction is highly endothermic, meaning it absorbs a significant amount of heat, leading to a temperature drop in the reactor bed. The mechanism primarily occurs on the metallic function (e.g., platinum sites) of the bifunctional catalyst and involves the sequential removal of hydrogen atoms from the naphthene ring. Given that naphthenes typically constitute a substantial portion of heavy naphtha feedstock (e.g., 30-40%), their efficient conversion to high-octane aromatics is paramount for achieving the primary objectives of the platforming process. The substantial production of hydrogen from this reaction further underscores its importance.

2.1.2. Dehydrocyclization of Paraffins to Aromatics

Dehydrocyclization is another crucial reaction that contributes to aromatics formation and hydrogen production, particularly from paraffinic components of the naphtha feed. This reaction converts linear or branched paraffins (alkanes) into aromatic hydrocarbons, also yielding hydrogen. An example is the conversion of n-heptane to toluene. $C_7H_{16} \text{ (n-heptane)} \rightarrow C_7H_8 \text{ (toluene)} + 4H_2$ The mechanism of dehydrocyclization is more complex than naphthene dehydrogenation. It is generally believed to involve the initial dehydrogenation of the paraffin to an olefin on a metal site, followed by the cyclization of the olefin to a naphthene intermediate on an acid site, and finally, the dehydrogenation of this naphthene to an aromatic hydrocarbon on a metal site. Thus, it effectively utilizes both the metal and acid functions of the catalyst. While paraffins constitute a large fraction of typical naphtha feedstock (e.g., 45-55%), they are generally more difficult to convert into aromatics compared to naphthenes. Therefore, optimizing catalyst formulation and operating conditions to promote dehydrocyclization is particularly important when processing paraffin-rich ("lean") naphthas to maximize the yield of high-value aromatics from the entire feedstock. This reaction is also endothermic.

2.1.3. Isomerization of Paraffins and Naphthenes

Isomerization reactions involve the rearrangement of the carbon skeleton of hydrocarbon molecules without changing their molecular weight, leading to the formation of isomers with different structural properties and, importantly, different octane numbers.

- **Paraffin Isomerization:** Linear paraffins (n-paraffins) are converted into their branched isomers (isoparaffins), which possess significantly higher octane ratings. For example, n-heptane can be isomerized to various isoheptanes. This reaction typically does not produce or consume hydrogen.
- **Naphthene Isomerization:** Five-carbon ring naphthenes (cyclopentanes) can be isomerized to six-carbon ring naphthenes (cyclohexanes). For instance, methylcyclopentane can isomerize to cyclohexane. This is often a precursor step, as cyclohexanes are more readily dehydrogenated to aromatics than cyclopentanes. These reactions primarily occur on the acid function of the catalyst and involve the formation of carbocation intermediates followed by skeletal rearrangement. Paraffin isomerization is a vital secondary reaction for octane improvement, particularly for the paraffinic components that are not converted via dehydrocyclization. Since the reformate product still contains a considerable amount of paraffins (e.g., 30-50%), ensuring that these remaining paraffins are in their higher-octane branched forms is crucial for the overall quality of the reformate. The hydrogen-neutral nature of paraffin isomerization means it enhances octane without affecting the overall hydrogen balance of the unit.

2.1.4. Hydrocracking of Paraffins

Hydrocracking involves the cleavage of carbon-carbon bonds in paraffin molecules, resulting in the formation of smaller, lower molecular weight hydrocarbons. This reaction consumes hydrogen. $C_{n}H_{2n+2} + H_2 \rightarrow C_{x}H_{2x+2} + C_{y}H_{2y+2} \text{ (where x+y=n)}$ In the context of platforming, hydrocracking is generally considered an undesirable side reaction because it reduces the yield of valuable gasoline-range reformate (C5+ hydrocarbons) and leads to the production of lighter products such as Liquefied Petroleum Gas (LPG: C3-C4) and fuel gas (C1-C2). However, some degree of controlled hydrocracking of very low-octane normal paraffins can be beneficial for overall octane improvement. Hydrocracking reactions can occur on both the metal sites and strong acid sites of the catalyst. The extent of hydrocracking must be carefully controlled by judicious catalyst design (particularly managing the strength and concentration of acid sites) and by optimizing operating conditions (such as temperature, pressure, and hydrogen partial pressure) to strike a balance between octane enhancement and the preservation of liquid product yield. With fresh, highly active catalysts, there can be a risk of "runaway hydrocracking," which is a highly exothermic and potentially uncontrolled reaction. This highlights the need for careful temperature control and catalyst activity management, especially during start-up phases. The production of LPG, while a yield loss for gasoline, contributes to the refinery's overall LPG pool.

2.2. Thermodynamics and Kinetics Overview

The thermodynamics of platforming reactions significantly influence process design and operation. The principal aromatics-producing reactions—dehydrogenation of naphthenes and dehydrocyclization of paraffins—are highly endothermic, requiring substantial heat input to drive them forward and maintain reaction temperatures. This endothermicity necessitates a reactor system typically comprising multiple adiabatic reactor beds arranged in series, with interstage heaters to reheat the process stream between reactors. This design ensures that the temperature, a critical parameter for reaction rates and equilibrium conversions, is maintained within the optimal range throughout the catalytic beds. Managing these temperature profiles is crucial for maximizing the conversion of reactants and the selectivity towards desired high-octane products. The significant energy consumption associated with interheating is a major factor in the operating costs of a platforming unit.

Isomerization reactions are generally characterized by mild exothermicity or endothermicity and are often equilibrium-limited within the typical operating temperature range of platforming units. Hydrocracking reactions, on the other hand, are typically exothermic. The heat released from hydrocracking can partially offset the endothermic heat demand of the aromatization reactions, but excessive hydrocracking can lead to temperature control challenges, especially the "runaway" phenomenon with highly active catalysts.

The kinetics of platforming reactions are complex, influenced by temperature, pressure, hydrogen partial pressure, catalyst activity, and feedstock composition. Higher temperatures generally increase reaction rates but can also promote undesirable side reactions like cracking and coke formation. Lower pressures and higher hydrogen-to-hydrocarbon ratios generally favor aromatization reactions and suppress coke formation, but lower pressures can also reduce throughput for a given reactor volume.

Fundamental kinetic models, such as the one developed by Sotelo-Boyas and Froment for Pt-Sn/Al_2O_3 catalysts, have been instrumental in understanding the intricate network of elementary steps occurring on both the metal and acid sites of the catalyst. These models, often based on single-event kinetics or detailed lumping schemes, allow for the prediction of product yields, catalyst deactivation rates, and overall process performance under various operating conditions. Such detailed kinetic understanding is essential for effective process optimization, the design of more efficient catalysts, advanced reactor engineering, and the development of robust process control strategies. These models help refiners to fine-tune operations to meet specific product quality targets (e.g., maximizing aromatics yield versus overall reformate octane) while managing catalyst life and energy consumption.

2.3. Typical Feedstock Characteristics and Product Compositions

The typical feedstock for the platforming process is heavy naphtha, a fraction obtained from the atmospheric distillation of crude oil, generally boiling in the range of approximately 80°C to 200°C. Light naphtha, containing hydrocarbons with six or fewer carbon atoms, is less suitable as these smaller molecules tend to crack into butane and lower molecular weight hydrocarbons, which are not useful as high-octane gasoline blending components.

The composition of heavy naphtha feedstock can vary significantly depending on the crude oil source, but a representative composition includes :

- Paraffins: 45-55% (by volume or weight)
- Naphthenes: 30-40%
- Aromatics: 5-10%

The ease of reforming is heavily dependent on this composition. Naphthas rich in naphthenes ("rich naphtha") are generally easier to process and yield more aromatics and hydrogen compared to naphthas with a high paraffin content ("lean naphtha"), which require more severe operating conditions.

Prior to entering the platforming unit, the naphtha feedstock undergoes extensive hydrotreating. This pretreatment step is crucial to remove impurities, particularly sulfur and nitrogen compounds, down to very low levels (typically <1 ppm for sulfur). These compounds are severe poisons for the noble metal catalysts used in platforming, and their removal is essential for maintaining catalyst activity and longevity. The effectiveness of the upstream hydrotreating unit, therefore, directly impacts the performance and economics of the platforming operation.

The platforming process significantly alters the chemical composition of the naphtha, resulting in a high-octane product known as reformate. A typical composition of the reformate (high-octane gasoline) is :

- Paraffins: 30-50% (now including more isoparaffins)
- Naphthenes: 5-10% (significantly reduced)
- Aromatics: 45-60% (substantially increased)

This compositional shift, particularly the dramatic increase in aromatic content and the conversion of linear paraffins to isoparaffins, is directly responsible for the significant boost in the octane number of the product stream. The reduction in naphthene content reflects their conversion into aromatics.

The quality of the feedstock, especially its naphthene versus paraffin content and the concentration of potential catalyst poisons, profoundly influences the required processing severity, the rate of catalyst deactivation, and the ultimate yields of reformate, aromatics, and hydrogen. This makes careful feedstock selection, rigorous pretreatment, and tailored operating strategies critical for optimizing the performance of the platforming unit.

Table 2.1: Typical Feedstock (Heavy Naphtha) and Product (Reformate) Compositions

Hydrocarbon Type	Feedstock (Heavy Naphtha) (vol%)	Product (Reformate) (vol%)	Typical Research Octane Number (RON) - Feed	Typical Research Octane Number (RON) - Product
Paraffins	45-55	30-50	40-60 (n-paraffins)	70-90 (mix of n- and iso-paraffins)
Naphthenes	30-40	5-10	60-80	(Largely converted)
Aromatics	5-10	45-60	100-115	100-115
Overall	**100**	**100**	**50-70**	**95-105+**
Data sourced and synthesized from. Octane numbers are representative ranges.				

This table clearly illustrates the chemical transformation achieved by the platforming unit. The substantial increase in the aromatics fraction, coupled with the isomerization of paraffins (reflected in the overall paraffin content but with a higher proportion of isoparaffins in the product), directly accounts for the significant enhancement in the Research Octane Number

(RON) from the typical feedstock range of 50-70 to the product reformate range of 95-105 or higher. This transformation is central to platforming's primary role in producing high-quality gasoline.

3. Platforming Catalysts: Design, Function, and Management

The heart of the platforming process lies in its specialized catalyst system. These catalysts are meticulously designed to promote the desired chemical reactions while minimizing undesirable side reactions and resisting deactivation under demanding process conditions.

3.1. Catalyst Composition and Structure

Platforming catalysts are typically bifunctional, meaning they possess two distinct types of active sites: metallic sites and acidic sites. The most common formulations consist of one or more noble metals, primarily platinum (Pt), dispersed on a high-surface-area, porous support material, which is almost universally a form of alumina (Al_2O_3), specifically gamma-alumina ($\gamma-\text{Al}_2\text{O}_3$). The platinum content is generally low, in the range of 0.3 to 0.6 wt%.

To enhance performance, platinum is often combined with one or more promoter metals. Common promoters include rhenium (Re), tin (Sn), and iridium (Ir). These promoters are added to improve various aspects of catalyst performance, such as activity, selectivity towards desired products (especially aromatics), stability against deactivation (e.g., coke formation or sintering), and regenerability. For instance, Pt-Re catalysts are known for their enhanced stability and ability to operate at lower pressures, while Pt-Sn catalysts can offer improved yields and coke suppression. Pt-Ir catalysts are often noted for increased activity. The Axens' Symphony® series of catalysts, for example, are described as multipromoted systems containing Pt/Sn or Pt/Re on alumina supports, tailored for specific applications like gasoline or aromatics production in CCR or semi-regenerative units.

Chloride is another critical component of platforming catalysts. It is intentionally added to the alumina support (resulting in "chlorinated alumina") to create and maintain the necessary acidity for certain reforming reactions. The chloride content is carefully controlled, as it influences the strength and number of acid sites, which are vital for isomerization and dehydrocyclization reactions. Continuous or periodic injection of a chlorinating agent (e.g., carbon tetrachloride or ethylene dichloride) into the feed or recycle gas is often practiced to maintain the optimal chloride level on the catalyst, compensating for any chloride stripping that may occur during operation or regeneration.

The evolution from early monometallic Pt catalysts to the current generation of bimetallic (e.g., Pt-Re, Pt-Sn) and sometimes trimetallic catalysts reflects a sophisticated and ongoing effort in catalyst design. This progression aims to achieve a delicate balance of multiple performance characteristics. The introduction of promoters like rhenium was driven by the need for catalysts that could maintain stability and activity at lower operating pressures, which are thermodynamically more favorable for reformate and hydrogen yields but can accelerate coke formation on simpler Pt catalysts. Tin was introduced to further improve selectivity and resistance to coking, particularly in CCR operations. Iridium has been used to boost overall activity. This targeted approach allows refiners to select catalysts optimized for their specific feedstock properties, desired product slate (e.g., maximum octane for gasoline pool vs.

maximum aromatics for petrochemicals), and operating conditions. The use of multiple promoters, as seen in Axens' Symphony® catalyst line , indicates a complex interplay of metallic functions designed to achieve superior overall performance.

Effective chloride management is a crucial aspect of operating platforming units. While chloride is essential for creating the acid sites necessary for key isomerization and cyclization reactions, its presence also poses challenges. The acidity must be carefully balanced: insufficient acidity leads to poor isomerization and cyclization activity, while excessive acidity can promote undesirable hydrocracking and accelerate coke formation. Moreover, chloride can be stripped from the catalyst by water or other compounds in the process stream and can subsequently form hydrochloric acid (HCl) in downstream sections of the unit. This HCl can cause significant corrosion problems in heat exchangers, piping, and other equipment, particularly if water is present to allow for aqueous phase corrosion or chloride stress corrosion cracking. Therefore, continuous monitoring and control of chloride levels on the catalyst and in the process streams are vital. This often involves the controlled addition of a chlorinating agent during operation and specific chlorination steps during catalyst regeneration, as well as the use of downstream chloride removal systems, such as UOP's Chlorsorb™ technology or Axens' chloride removal adsorbents , to protect equipment and maintain process integrity.

Table 3.1: Key Platforming Catalyst Formulations and Component Roles

Metal Component(s)	Support	Promoter/Additive	Typical Concentration Range (wt% of metal(s))	Primary Role(s)
Platinum (Pt)	\gamma-\text{Al}_2\text{O}_3	Chloride	0.2 - 0.7	Primary metal function (dehydrogenation, hydrogenation), some hydrogenolysis
Pt, Rhenium (Re)	\gamma-\text{Al}_2\text{O}_3	Chloride	Pt: 0.2-0.6, Re: 0.2-0.6	Pt: Metal function. Re: Enhances stability, activity maintenance, coke suppression, sulfur resistance
Pt, Tin (Sn)	\gamma-\text{Al}_2\text{O}_3	Chloride	Pt: 0.2-0.6, Sn: variable (often < Pt)	Pt: Metal function. Sn: Improves selectivity, reduces coke, enhances stability, particularly in CCR
Pt, Iridium (Ir)	\gamma-\text{Al}_2\text{O}_3	Chloride	Pt: 0.2-0.6, Ir: variable	Pt: Metal function. Ir: Boosts activity
Alumina (\text{Al}_2\text{O}_3)	-	Chloride	Support material	Provides high surface area for metal dispersion, contributes acid sites when

Metal Component(s)	Support	Promoter/Additive	Typical Concentration Range (wt% of metal(s))	Primary Role(s)
				chlorided
Chloride (Cl)	On Alumina	-	0.3 - 1.0 (on catalyst)	Creates and maintains acid sites on alumina support, crucial for isomerization and cyclization
Data synthesized from. Concentration ranges are typical and can vary by specific catalyst formulation and licensor.				

This table provides a structured overview of common platforming catalyst components and their primary functions. It highlights how different metals and additives are combined to create a catalyst system optimized for the complex chemical transformations required in the platforming process. Understanding these roles is key to appreciating the advanced material science involved in modern catalyst design.

3.2. The Bifunctional Nature of Platforming Catalysts: Metal and Acid Functions

Platforming catalysts are classic examples of bifunctional catalysts, possessing two distinct types of active centers that work in concert to achieve the desired hydrocarbon transformations.

- **Metal Function:** This is provided by the dispersed noble metal particles, primarily platinum and its promoters (Re, Sn, Ir). The metal sites are responsible for hydrogenation and dehydrogenation reactions. Key reactions catalyzed by the metal function include the dehydrogenation of naphthenes to aromatics, the initial dehydrogenation of paraffins to olefins (a step in dehydrocyclization), and the final dehydrogenation of cyclized intermediates to aromatics. Hydrogenation activity is also important, for example, in saturating coke precursors or in hydrocracking reactions.
- **Acid Function:** This is provided by the catalyst support, typically chlorinated alumina (\text{Al}_2\text{O}_3). The interaction of chloride with the alumina surface creates Brønsted and Lewis acid sites. These acid sites catalyze reactions involving carbocation intermediates, such as the isomerization of paraffins (n-paraffins to isoparaffins) and naphthenes (e.g., five-membered rings to six-membered rings), and the cyclization step in the dehydrocyclization of paraffins (olefins to naphthenes). Stronger acid sites can also contribute to hydrocracking reactions.

The synergy between these two functions is fundamental to the success of the platforming process. Many of the desired overall reactions, such as the dehydrocyclization of paraffins to aromatics, require a sequence of steps that alternate between metal-catalyzed and acid-catalyzed transformations. For example, a paraffin molecule might first be dehydrogenated to an olefin on a metal site; this olefin could then migrate to an acid site where it undergoes cyclization to form a naphthene; finally, the naphthene could migrate back to a metal site for dehydrogenation to an aromatic. For this sequence to occur efficiently, the metal and acid sites must be in close proximity and their respective activities must be appropriately balanced. An imbalance, such as excessively strong acidity relative to metal activity, could lead to an overproduction of cracked products and coke, rather than the desired aromatics and isomers. The design of platforming catalysts, therefore, involves careful control over not only the type and amount of metal(s) but also the properties of the support, particularly its acidity. The acidity is fine-tuned by controlling the alumina's characteristics (e.g., surface area, pore structure) and, critically, the amount of chloride incorporated and maintained on its surface. Too little acidity will result in poor isomerization and cyclization activity, leading to lower reformate octane. Conversely, too much acidity can lead to excessive hydrocracking, which reduces the yield of valuable gasoline-range products and consumes hydrogen, and can also accelerate the rate of coke formation, leading to faster catalyst deactivation. This delicate balance is a key focus of catalyst manufacturers and refinery operators.

3.3. Role of Promoters (e.g., Re, Sn, Ir) in Enhancing Performance

The addition of secondary or tertiary metallic components (promoters) to the primary platinum catalyst significantly enhances its performance in various ways. These promoters are not merely diluents but actively participate in modifying the catalyst's properties and behavior.

- **Rhenium (Re):** When added to platinum, rhenium forms bimetallic Pt-Re clusters or alloys. One of the primary benefits of Re is improved catalyst stability and resistance to deactivation, particularly by coke. This enhanced stability allows Pt-Re catalysts to operate for longer periods between regenerations or to be used under more severe conditions (e.g., lower pressures, which are thermodynamically favorable for product yields but can accelerate coking on unpromoted Pt catalysts). Rhenium is thought to modify the electronic properties of platinum, potentially reducing the strength of adsorption of coke precursors and thereby inhibiting their growth into deactivating coke deposits. Additionally, Re can improve the redispersion of platinum during regeneration cycles. Some studies suggest Re helps maintain Pt dispersion by inhibiting sintering. Another important role attributed to rhenium is its ability to confer some sulfur tolerance or to protect platinum from sulfur poisoning by preferentially adsorbing sulfur compounds. In analogous reforming reactions like glycerol reforming, Re has been shown to reduce the binding energy of CO to Pt, inhibit nanoparticle sintering, and facilitate water-gas shift and CO bond cleavage reactions, all contributing to enhanced overall rates. In hydrodeoxygenation (HDO) reactions, Re-oxide species are crucial for the deoxygenation step, working synergistically with Pt's hydrogenation function.
- **Tin (Sn):** Tin is another widely used promoter, especially in catalysts designed for CCR units operating at low pressures. Pt-Sn catalysts exhibit improved selectivity towards aromatics and isoparaffins, and significantly enhanced resistance to coke formation. The mechanisms by which Sn imparts these benefits are believed to be both geometric and electronic. Geometrically, Sn atoms can dilute Pt surface ensembles, breaking up large Pt sites that are thought to be active for coke-forming reactions (e.g., deep dehydrogenation and polymerization of olefins). Sn may also preferentially occupy low-coordination Pt sites (like corners and edges) that are particularly prone to initiating coke. Electronically, Sn can donate electrons to Pt, modifying its electronic structure. This electronic modification is

thought to weaken the adsorption of hydrocarbons, particularly olefins and other coke precursors, on the Pt sites, thus reducing their surface residence time and the likelihood of their conversion to coke. The weakened binding of product alkenes also facilitates their desorption, improving selectivity. Sn also helps to retard the sintering of Pt particles.
- **Iridium (Ir):** Iridium has been used as a promoter in some platforming catalysts, primarily to boost overall catalytic activity. Pt-Ir catalysts can exhibit higher initial activity for reforming reactions. Iridium is known for its high intrinsic activity in various catalytic reactions and its resistance to corrosion. However, managing the stability and interaction between Pt and Ir to prevent issues like selective coking or phase separation can be challenging.

The use of these promoters illustrates the complexity of modern platforming catalyst design. They are not just simple mixtures but often involve the formation of specific bimetallic or multimetallic nanoparticles or alloy structures where the intimate interaction between platinum and the promoter metal(s) is critical for achieving the desired synergistic effects. For example, the electron transfer from Sn to Pt, or the specific cluster formation in Pt-Re systems, are key to their enhanced performance. This means that the catalyst preparation methods must be carefully controlled to ensure the optimal dispersion, composition, and structure of these metallic phases on the support. The choice of promoter and its concentration is a strategic decision made by catalyst manufacturers and refiners, based on the specific feedstock characteristics, desired product slate (e.g., maximizing aromatics for petrochemicals versus maximizing overall reformate octane for gasoline), operating conditions of the unit, and the primary deactivation challenges anticipated (e.g., high coking tendency of the feed, presence of trace poisons).

3.4. Catalyst Deactivation Mechanisms

Despite sophisticated design, platforming catalysts gradually lose their activity and/or selectivity during operation. This deactivation is an inevitable consequence of the harsh reaction environment and the nature of the chemical transformations occurring. The primary mechanisms responsible for catalyst deactivation in platforming units are coke deposition, poisoning by feed impurities, and thermal degradation (sintering). Understanding these mechanisms is crucial for optimizing operating conditions, developing effective regeneration procedures, and designing more robust catalysts. Catalyst deactivation directly impacts the operational efficiency of the unit, shortens run lengths between regenerations (for semi-regenerative units), and influences overall process economics due to the costs associated with regeneration, catalyst replacement, and potential production losses during downtime. The development of different reforming technologies (SRR, Cyclic, CCR) has been largely driven by the need to manage catalyst deactivation more effectively.

3.4.1. Coke Deposition: Formation, Effects, and Mitigation

Coke deposition is the most common and significant cause of deactivation for platforming catalysts. "Coke" refers to carbonaceous polymeric materials that deposit on the catalyst surface, physically blocking active metal and acid sites, and potentially obstructing catalyst pores. This blockage reduces the number of sites available for reaction and can hinder the diffusion of reactants to, and products from, the active sites, leading to a decline in conversion and selectivity. Severe coking can also lead to an increased pressure drop across the reactor bed.

Coke formation is a complex process involving a series of reactions of hydrocarbon intermediates on the catalyst surface. It is generally favored by conditions such as high temperatures, low hydrogen partial pressures (or low hydrogen-to-hydrocarbon ratios), and the presence of highly unsaturated hydrocarbons (e.g., olefins, diolefins, and polyaromatics) in the feed or formed as intermediates. Both metal and acid sites can contribute to coke formation. Metal sites can catalyze deep dehydrogenation and polymerization reactions, while strong acid sites can promote condensation and polymerization of unsaturated species.

Strategies to mitigate coke deposition include:

1. **Optimizing Operating Conditions:** Maintaining an adequate hydrogen partial pressure is critical, as hydrogen inhibits coke formation by hydrogenating coke precursors and promoting their desorption. Controlling reactor temperatures within the optimal range also helps, as excessively high temperatures accelerate coking rates.
2. **Catalyst Design:** Incorporating promoters like tin (Sn) or rhenium (Re) into platinum-based catalysts can significantly reduce coke formation by modifying the electronic and geometric properties of the platinum sites, making them less prone to catalyzing coke-forming reactions. The acidity of the support is also carefully controlled to minimize acid-catalyzed coking.
3. **Feedstock Selection and Pretreatment:** Using cleaner feedstocks with lower concentrations of coke precursors (e.g., olefins, heavy aromatics) can reduce the coking tendency.
4. **Regular Regeneration:** The primary method for dealing with coke is periodic or continuous regeneration, during which the coke is burned off the catalyst in a controlled manner.

Coke management is a central theme in platforming technology. The entire design philosophy of Continuous Catalyst Regeneration (CCR) systems revolves around continuously removing coke from a portion of the catalyst inventory, allowing the unit to operate with a highly active catalyst at all times and under conditions (e.g., low pressure) that would otherwise lead to rapid coking in fixed-bed systems.

3.4.2. Poisoning (e.g., by Sulfur, Nitrogen, Metals)

Platforming catalysts, particularly the noble metal components, are highly susceptible to poisoning by various impurities present in the naphtha feedstock.

- **Sulfur Compounds:** Sulfur, typically present as thiols, sulfides, or thiophenes in untreated naphtha, is a severe poison for platinum and rhenium. Sulfur atoms strongly chemisorb on the metal surfaces, blocking active sites and altering the electronic properties of the metal, thereby reducing its catalytic activity for dehydrogenation and other desired reactions. Even at parts-per-million (ppm) levels, sulfur can cause significant deactivation. This is why naphtha feed to platformers is rigorously hydrodesulfurized (HDS) to reduce sulfur content to sub-ppm levels. Some promoters, like rhenium, are reported to offer a degree of protection to platinum by preferentially adsorbing sulfur.
- **Nitrogen Compounds:** Organic nitrogen compounds (e.g., pyridines, quinolines) in the feed can also act as poisons. These basic compounds tend to neutralize the acid sites on the alumina support, thereby reducing the catalyst's activity for isomerization and cyclization reactions. Like sulfur, nitrogen compounds are removed by hydrodenitrogenation (HDN) during feed pretreatment.
- **Metals:** Trace metals such as arsenic, lead, and copper, if present in the feedstock, can

deposit on the catalyst and cause irreversible deactivation by physically blocking sites or alloying with the active metals. These are typically removed in the hydrotreater guard beds or by specific adsorbent beds if necessary.

The critical importance of feed pretreatment cannot be overstated. The efficiency and reliability of the upstream hydrotreating unit directly dictate the performance, cycle length, and overall lifespan of the much more expensive and sensitive platforming catalyst. Any upset or inefficiency in the hydrotreater that allows even trace amounts of poisons to slip into the platformer can have severe and costly consequences. This strong interdependence between units is a key consideration in refinery operations and optimization. The ongoing drive in catalyst research includes developing catalysts that are more tolerant to these poisons, which could potentially reduce the stringency (and cost) of feed pretreatment or allow for the processing of more challenging, contaminated feedstocks.

3.4.3. Sintering and Thermal Degradation

Sintering refers to the agglomeration of small, highly dispersed metal crystallites (e.g., platinum particles) into larger particles at elevated temperatures. This process leads to a decrease in the active metal surface area exposed to the reactants and, consequently, a loss of catalytic activity. Sintering is a form of thermal degradation and is generally irreversible. The high temperatures experienced by the catalyst, particularly during the coke combustion step of regeneration (which can be highly exothermic if not properly controlled), are the primary drivers for sintering. Water vapor, often present during regeneration or due to process upsets, can also accelerate sintering rates. The catalyst support material (alumina) can also undergo thermal degradation, such as loss of surface area or changes in pore structure (e.g., collapse of micropores), at very high temperatures, although this is generally less of a concern than metal sintering under typical platforming conditions. Strategies to mitigate sintering include:

1. **Careful Control of Regeneration Conditions:** Strict control of temperature, oxygen concentration, and moisture levels during the coke burn-off step is essential to prevent localized overheating and minimize thermal stress on the catalyst.
2. **Catalyst Design:** Incorporating promoters can help to stabilize the metal dispersion and inhibit sintering. For example, rhenium and tin are known to improve the thermal stability of platinum particles by forming bimetallic clusters or alloys that are more resistant to agglomeration than pure platinum. The interaction between the metal particles and the support also plays a role in anchoring the particles and preventing their migration and coalescence. Sintering represents a permanent loss of active sites and is a key factor limiting the ultimate lifespan of a platforming catalyst. While regeneration can restore activity lost due to coking, it cannot reverse deactivation caused by sintering. Therefore, maximizing catalyst life involves not only effective coke removal but also minimizing the conditions that promote sintering during both operation and regeneration.

3.5. Catalyst Regeneration: Processes and Best Practices

Catalyst regeneration is a critical and complex operation in platforming, designed to restore the activity of catalysts that have been deactivated, primarily by coke deposition. The regeneration process also typically includes steps to adjust the chloride content on the catalyst to maintain optimal acidity and to ensure the active metals are in the correct state for catalytic activity. The frequency and method of regeneration depend on the type of platforming technology employed (SRR, Cyclic, or CCR).

The regeneration procedure generally involves several distinct steps :

1. **Coke Burn-off:** This is the primary step, where the accumulated coke deposits are removed from the catalyst by controlled combustion (oxidation) with an oxygen-containing gas (typically air diluted with nitrogen or flue gas). This is a highly exothermic process, and careful control of temperature and oxygen concentration is paramount to prevent excessive temperature excursions that could lead to catalyst sintering and permanent damage. Oxygen and moisture levels in the regeneration gas are closely monitored to optimize the burn rate and manage heat release.
2. **Chlorination (Oxychlorination):** After coke removal, a chlorination step is often performed to replenish any chloride lost from the alumina support during operation or the coke burn, and to ensure the proper redispersion of the platinum group metals. This step involves contacting the catalyst with a controlled amount of a chlorinating agent (e.g., HCl, carbon tetrachloride, or an organic chloride) in the presence of oxygen at elevated temperatures. This restores the catalyst's acidity, which is crucial for isomerization and cyclization reactions, and helps to redisperse sintered metal particles, partially recovering lost metal surface area.
3. **Drying:** Following chlorination, the catalyst may be dried to remove residual moisture. Proper drying is important, especially in CCR units where catalyst must flow smoothly.
4. **Reduction:** The final step is typically a reduction of the oxidized metal components (platinum and promoters) back to their active metallic state. This is usually carried out by contacting the catalyst with hydrogen at a controlled temperature.

In **Semi-Regenerative Reformers (SRR)** and **Cyclic Reformers**, regeneration is performed *in-situ* within the reactors. For SRR units, this requires a complete shutdown of the unit every 6 to 24 months. Cyclic reformers use a swing reactor, allowing one reactor to be taken offline for regeneration while the others continue to operate, thus improving the overall on-stream factor compared to SRR.

Continuous Catalyst Regeneration (CCR) technology represents a significant advancement by integrating the regeneration process into continuous operation. A portion of the catalyst is continuously withdrawn from the last reactor, transferred to a dedicated regeneration vessel where it undergoes the coke burn, chlorination, drying, and reduction steps, and then returned to the first reactor. This allows the reaction section to operate with catalyst at a consistently high activity level. CCR units can therefore operate at more severe conditions (e.g., lower pressures) that maximize desired product yields and octane, as coke formation is continuously managed. However, CCR systems introduce mechanical complexity associated with catalyst circulation (lifts, valves, seals) and require highly reliable and efficient regeneration tower designs (e.g., UOP's CycleMax , Axens' RegenC-2).

The efficiency of the regeneration process directly impacts catalyst lifespan, overall process economics, and the environmental footprint of the platforming unit. Each step must be meticulously controlled to fully restore catalyst activity without causing thermal or chemical damage. Best practices involve precise temperature programming, careful management of gas compositions (oxygen, chlorine, hydrogen, moisture), and robust monitoring systems to ensure optimal regeneration and maximize the value derived from the catalyst inventory.

4. Platforming Process Technologies

The evolution of platforming technology has led to distinct process configurations, primarily differentiated by their approach to catalyst regeneration. These are broadly categorized as

Semi-Regenerative Reforming (SRR), Cyclic Reforming, and Continuous Catalyst Regeneration (CCR) Reforming.

4.1. Semi-Regenerative Reforming (SRR)

Semi-Regenerative Reforming is the original and simplest type of catalytic reforming process. SRR units typically consist of three or four fixed-bed reactors operating in series, with interheaters between the reactors to supply the endothermic heat of reaction. The catalyst remains in the reactors for an entire operating cycle, which can last from 6 to 24 months, depending on the feedstock, operating severity, and catalyst type. During the operating cycle, catalyst activity gradually declines due to coke deposition and, to a lesser extent, chloride loss or sintering. To maintain the desired product octane, the reactor temperatures are progressively increased. When the catalyst activity drops to a point where further temperature increases are impractical or uneconomical, or when the maximum allowable temperature is reached, the entire unit must be shut down for *in-situ* catalyst regeneration. To minimize the rate of coke formation and extend the cycle length between regenerations, SRR units traditionally operate at relatively high pressures (e.g., 200-300 psig or ~15-20 barg) compared to CCR units. While higher pressure reduces coking, it is thermodynamically unfavorable for the desired dehydrogenation and dehydrocyclization reactions, leading to lower reformate and hydrogen yields compared to lower-pressure operations. Pt-Re catalysts are commonly used in SRR units due to their good stability and tolerance to coke. SRR units can typically achieve reformate octane numbers in the range of 85-100 RONC. SRR technology is mature and characterized by a simpler design and operation compared to CCR systems, involving lower initial capital investment. However, the periodic shutdowns for regeneration reduce the overall on-stream factor and can lead to production losses. The higher operating pressure also results in inherently lower yields of high-value products. Consequently, while SRR units are still in operation, particularly in smaller refineries or specific economic contexts where the higher investment for CCR cannot be justified, they are increasingly being converted to or replaced by CCR technology, especially for larger capacities or when higher severity and yields are paramount. Axens, for instance, still offers SRR technology specifically for lower-capacity units.

4.2. Cyclic Reforming

Cyclic Reforming technology was developed as an improvement over SRR to enhance the on-stream factor. These units typically employ an additional "swing" reactor, allowing one reactor in the system to be taken offline for regeneration while the other reactors (usually three or four) remain in operation, processing feed. Once the catalyst in the swing reactor is regenerated, it is brought back online, and another reactor with deactivated catalyst is taken offline and switched into regeneration mode. This "cyclic" regeneration of individual reactors extends the period between complete unit shutdowns. Cyclic reformers can operate at somewhat more severe conditions (e.g., lower pressures, around 200 psig or ~14 barg) than SRR units because the regeneration frequency for any given reactor is higher (weeks to months, rather than many months to years). This allows for the production of higher octane reformate, typically in the range of 100-104 RONC. However, cyclic reforming units are mechanically more complex than SRR units due to the intricate piping and valve systems required for isolating and switching reactors between reaction and regeneration modes. This complexity can lead to higher maintenance requirements and potential operational challenges. While cyclic reforming offered an advantage in on-stream time over SRR, it is generally considered less common or "least in terms of utilization" compared to both SRR and the more advanced CCR technology , largely because CCR technology provides even greater operational flexibility and yield benefits.

4.3. Continuous Catalyst Regeneration (CCR) Reforming

Continuous Catalyst Regeneration (CCR) Reforming represents the state-of-the-art in platforming technology and is the preferred choice for most new reforming units and major revamps. In a CCR system, the catalyst continuously circulates as a slowly moving bed through a series of stacked or side-by-side reactors and then passes to a dedicated, external regeneration vessel where a portion of the catalyst inventory is continuously regenerated. The regenerated catalyst is then returned to the top of the first reactor. This continuous movement and regeneration cycle ensures that the reactors always operate with catalyst at a consistently high level of activity. The key advantage of CCR technology is its ability to operate at significantly lower pressures (e.g., 50-150 psig or ~3.5-10 barg) and higher severities than SRR or cyclic units. Low-pressure operation is thermodynamically favorable for the desired dehydrogenation and dehydrocyclization reactions, leading to substantially higher yields of reformate (C5+) and hydrogen, as well as higher reformate octane numbers (typically 95-108 RONC or even higher for aromatics production mode). The continuous removal of coke prevents severe catalyst deactivation, allowing for sustained high-severity operation. Leading licensors such as Honeywell UOP (with its CCR Platforming™ process, featuring the CycleMax™ regenerator and specialized catalysts like the R-264 series) and Axens (with its Octanizing™ and Aromizing™ processes, featuring the RegenC-2™ regenerator and Symphony® series catalysts) have developed highly sophisticated CCR systems. These systems incorporate advanced designs for catalyst handling (e.g., gentle lift systems to minimize attrition), efficient regenerators for complete coke combustion and metal redispersion, and optimized reactor internals. Critical aspects of CCR operation include precise control of the regeneration process, particularly oxygen and moisture levels during coke burning, to maximize catalyst life and performance. Managing operations when the unit produces low levels of coke on the catalyst (e.g., due to very clean feed or low severity operation) can also present unique challenges for the regeneration section, sometimes requiring special operating modes like "Grey Burn" or "Black Burn" to maintain regenerator stability and efficiency. The sophistication of CCR systems, including the catalyst circulation mechanisms and the advanced regenerator designs, reflects significant research and development efforts by technology licensors. These innovations aim to address challenges such as catalyst attrition, fines production, ensuring uniform catalyst flow and regeneration, and optimizing energy efficiency. This ongoing development is crucial for maintaining a competitive edge and meeting the evolving needs of refineries for higher yields, better product quality, and longer operational campaigns.

4.4. Comparative Analysis of Reforming Technologies

The choice between SRR, Cyclic, and CCR reforming technologies depends on various factors, including refinery capacity, investment capital availability, desired product slate and quality, and hydrogen requirements. However, a comparative analysis reveals distinct advantages for CCR technology in most modern applications.

Table 4.1: Comparative Analysis of Reforming Technologies

Feature	Semi-Regenerative (SRR)	Cyclic Reforming	Continuous Catalyst Regeneration (CCR)
Catalyst System	Fixed-Bed	Fixed-Bed (with Swing Reactor)	Moving-Bed
Regeneration Mode	In-situ, Unit Shutdown Required	In-situ, One Reactor at a Time (Continuous Ops)	External, Continuous
Operating Pressure	Higher (e.g., 15-20 barg / 200-300 psig)	Moderate (e.g., ~14 barg / ~200 psig)	Lower (e.g., 3.5-10 barg / 50-150 psig)
Operating Temperature	480-525 °C	515-520 °C	515-530 °C
Typical Reformate Octane (RONC)	85-100	100-104	95-108+
Hydrogen Yield	Lower	Moderate	Higher
Reformate (C5+) Yield	Lower	Moderate	Higher
Catalyst Cycle Length	6-24 months	Weeks to Months (per reactor)	Continuous Regeneration (effectively infinite cycle)
On-Stream Factor	Lower (due to shutdowns)	Higher than SRR	Highest
Relative Capital Cost	Lowest	Moderate	Highest
Relative Operating Cost	Moderate (higher energy due to pressure)	Moderate to High (complexity)	Lower (energy benefits from low pressure)
Key Advantages	Simpler design, lower capital cost	Improved on-stream vs. SRR, higher severity possible	Max product yields & quality, max H_2, high on-stream factor, operational flexibility
Key Disadvantages	Periodic shutdowns, lower yields/octane, higher pressure operation	Complex valve switching, higher maintenance than SRR	Higher capital cost, mechanical complexity of catalyst handling
Data synthesized from sources including. Ranges are typical and can vary.			

The clear advantages of CCR technology in terms of superior product quality (higher octane), increased yields (both reformate and hydrogen), continuous operation (higher on-stream factor), and the ability to operate at higher severities make it the dominant choice for most modern refining applications. The thermodynamic benefits of low-pressure operation, enabled by continuous catalyst regeneration, are the primary driver for this superiority. While CCR units may involve higher initial capital investment and greater mechanical complexity compared to SRR units, the enhanced performance and operational flexibility typically result in better overall economics, particularly for large-scale units or refineries focused on maximizing the production of high-value reformate and hydrogen.

4.5. Leading Technology Licensors and Their Offerings

The platforming technology market, particularly for CCR systems, is characterized by a few major licensors who have developed proprietary processes, catalysts, and equipment designs.

- **Honeywell UOP:** A pioneering company in catalytic reforming, UOP commercialized the first CCR Platforming™ unit in 1971. Their CCR Platforming™ technology is a market leader, with a large number of operating units worldwide (191 operating and 37 in design/construction as of a 2005 report). Key features of UOP's offering include the CycleMax™ catalyst regenerator, known for its efficiency and ability to achieve long catalyst life; advanced catalyst families such as the R-264 series, designed for high activity, yield, and stability; and the Chlorsorb™ system for HCl removal from regenerator vent gas. UOP emphasizes designs for large capacity units, often employing stacked reactor configurations for reduced plot space and capital cost, and features for smooth catalyst movement to minimize attrition.
- **Axens:** Axens, an IFP Group company, is another major licensor of catalytic reforming technology. They offer a portfolio that includes Semi-Regenerative Reforming (for lower capacities, using their Symphony® multi-promoted catalysts), Cyclic Reforming, and advanced CCR processes. Their flagship CCR technologies are Octanizing™ (primarily for high-octane gasoline production) and Aromizing™ (optimized for aromatics production, often integrated into ParamaX® aromatics complexes). Axens highlights features such as side-by-side reactor arrangements, highly integrated energy optimization, and their proprietary RegenC-2™ continuous catalyst regenerator. Their Symphony® catalyst family includes various grades (e.g., PS, CR, AR, PR series) based on Pt/Sn or Pt/Re on alumina, tailored for different process types and objectives. Axens has licensed over 130 Octanizing™ and Aromizing™ units worldwide.
- **Chevron Lummus Global (CLG):** CLG, a joint venture between Chevron and Lummus Technology, is mentioned as a competitive technology provider in the continuous catalytic reforming reactor market. Their focus is reported to be on flexible licensing agreements and integrated process packages, which can be particularly beneficial for refiners looking to optimize retrofit projects. While Lummus Technology itself is strongly associated with hydrogen and synthesis gas technologies like Steam Methane Reforming (SMR) and Auto-Thermal Reforming (ATR) , CLG's ISOCRACKING™ hydrocracking technology is noted to produce heavy naphtha that is well-suited as a feedstock for catalytic reforming units. A Chevron patent also discusses reforming processes aimed at enhancing benzene purity using non-acidic catalysts.
- **KBR:** KBR is also listed as a technology provider in the continuous catalytic reforming reactor marketplace. Historically, KBR has been involved in various refining technologies, including catalytic reforming. KBR's differentiation in the current reforming market is cited as modular reactor designs and digital optimization platforms that aim to accelerate project commissioning and reduce operational risk. While many KBR-related snippets focus on technologies like ammonia synthesis (which uses steam reforming for syngas), Fluid Catalytic Cracking (FCC), and alkylation , a recent development mentions KBR's involvement in a project that includes continuous catalytic reforming units for Euro V gasoline and diesel production.

The dominance of UOP and Axens in licensing comprehensive CCR platforming packages, including proprietary catalysts and regeneration systems, indicates a market where significant R&D investment and deep process expertise are critical. Other players like CLG and KBR appear to offer specialized solutions, retrofitting expertise, or modular components within the broader reforming landscape. This competitive environment drives continuous innovation aimed at improving yields, energy efficiency, catalyst life, and operational reliability to meet the evolving demands of the refining industry.

5. Products of the Platforming Process

The platforming process transforms low-octane naphtha into a slate of valuable products, each serving distinct purposes within the refinery and the broader petrochemical industry. The primary liquid product is high-octane reformate, but significant quantities of aromatic hydrocarbons, hydrogen, and light ends (LPG) are also generated.

5.1. Reformate: Primary Gasoline Blending Stock

The principal product of the platforming process is reformate, a high-octane gasoline blending component. It is characterized by a significantly higher Research Octane Number (RON) and Motor Octane Number (MON) compared to the naphtha feed, making it essential for producing finished gasolines that meet the anti-knock requirements of modern internal combustion engines. The octane improvement is primarily due to the increased concentration of aromatic hydrocarbons and isoparaffins formed during the reforming reactions. Reformate quality is defined by several specifications, including octane numbers (RON typically 95-105+ for CCR products), aromatics content, benzene content, sulfur content (which should be extremely low due to hydrotreated feed), and Reid Vapor Pressure (RVP). These properties determine its suitability and value as a blending component in the refinery's gasoline pool. Analytical standards such as EN ISO 22854 and ASTM D6839 are used for detailed hydrocarbon group type analysis of reformate and gasoline. Reformate is a cornerstone for meeting overall gasoline pool octane specifications, especially crucial since the phase-out of lead additives and with increasing restrictions on other octane enhancers like MTBE in some regions. The blending characteristics of reformate, particularly its high aromatic content, significantly influence the properties of the final gasoline product.

5.2. Aromatic Hydrocarbons (BTX): Feedstock for Petrochemicals

Platforming units are a major source of aromatic hydrocarbons, specifically Benzene, Toluene, and Xylenes (collectively known as BTX). These aromatics are fundamental building blocks for the petrochemical industry, serving as raw materials for the production of a vast array of consumer and industrial goods, including plastics (e.g., polystyrene, PET), synthetic fibers (e.g., nylon, polyester), resins, solvents, and detergents. The concentration of BTX in the reformate can be maximized by adjusting feedstock selection (e.g., using naphtha cuts rich in C6-C8 naphthenes and paraffins) and operating conditions (higher severity). In refineries with integrated petrochemical complexes, the reformate stream may be routed to an aromatics extraction unit where BTX components are selectively separated from the non-aromatic portion of the reformate. The extracted BTX is then supplied to downstream petrochemical plants. Benzene management is a critical aspect of platforming operations due to its classification as a carcinogen and the stringent regulations limiting its concentration in finished gasoline. Refiners employ several strategies to manage benzene, including:

1. **Pre-fractionation of Feed:** Removing benzene precursors (cyclohexane,

methylcyclopentane) from the naphtha feed before it enters the reformer.
2. **Benzene Extraction from Reformate:** Separating benzene from the reformate stream for use as a chemical feedstock, thereby reducing its content in the gasoline blending pool.
3. **Benzene Saturation:** Hydrogenating the benzene in specific reformate cuts to convert it to cyclohexane. The production of BTX provides a significant revenue stream for refineries, linking their operations directly to the petrochemical value chain and offering diversification beyond transportation fuels.

5.3. Hydrogen: Valuable Byproduct

A significant and highly valuable byproduct of the platforming process is hydrogen gas (H_2). It is primarily produced from the dehydrogenation of naphthenes and the dehydrocyclization of paraffins. The net hydrogen production typically ranges from about 50 to 200 standard cubic meters per cubic meter of naphtha feedstock (approximately 300 to 1200 scf/bbl), depending on feedstock composition (higher naphthene content yields more hydrogen) and operating conditions. Platformer-derived hydrogen is generally of high purity and is a critical utility within the refinery. It is extensively used in various hydroprocessing units, such as:

- **Hydrotreating Units:** For the removal of sulfur (hydrodesulfurization, HDS), nitrogen (hydrodenitrogenation, HDN), oxygen, and metals from various refinery streams (e.g., naphtha, kerosene, diesel, gas oils). This is essential for producing clean fuels that meet environmental specifications and for protecting downstream catalysts from poisoning.
- **Hydrocracking Units:** For converting heavy, low-value gas oils and residues into lighter, more valuable products like gasoline, jet fuel, and diesel. Hydrocracking consumes large quantities of hydrogen.
- **Isomerization Units:** For isomerizing light naphtha to produce high-octane gasoline components. The platforming unit is often the primary source of hydrogen within a refinery, playing a crucial role in the overall "hydrogen balance." The availability of this internally produced hydrogen is vital for the refinery's ability to process heavier and more sour (higher sulfur) crude oils and to meet the increasingly stringent quality specifications for transportation fuels mandated by environmental regulations. In many cases, the hydrogen output from the platformer can be a limiting factor for a refinery's capacity to upgrade heavier fractions or to maximize the production of ultra-low sulfur fuels.

5.4. Liquefied Petroleum Gas (LPG)

Light hydrocarbons, primarily propane (C3) and butanes (C4), are produced as byproducts in the platforming process. These components, collectively referred to as Liquefied Petroleum Gas (LPG), mainly result from hydrocracking reactions that break down larger paraffin molecules into smaller ones. Methane (C1) and ethane (C2) are also produced and are typically routed to the refinery fuel gas system. The LPG fraction is separated from the reformate in a stabilization section, usually involving a distillation column. The recovered LPG can be used for several purposes:

- **Gasoline Blending:** Butanes, particularly n-butane and isobutane, can be blended into the gasoline pool to control its vapor pressure (RVP) and improve cold start performance, subject to seasonal and regional specifications.
- **Petrochemical Feedstock:** Propane and butanes are valuable feedstocks for steam crackers (producing ethylene and propylene) or for dehydrogenation units (producing

propylene and butylenes).
- **Fuel:** LPG can be sold as a fuel for residential, commercial, or industrial use, or used internally within the refinery as fuel.
- **Hydrogen Manufacturing Unit (HMU) Feed:** C1-C4 hydrocarbons can serve as feedstock for steam reformers to produce additional hydrogen. While LPG is generally a lower-value product compared to reformate and aromatics, its production contributes to the overall refinery product slate and can be a marketable commodity or a useful internal fuel/feedstock. The yield of LPG is directly influenced by the extent of hydrocracking reactions, which in turn depends on catalyst type (especially acidity), operating severity, and feedstock composition. Refineries aim to control hydrocracking to minimize the yield loss of the primary C5+ reformate while producing an economically optimal amount of LPG.

5.5. Typical Product Yields and Distribution

The yields of the various products from the platforming process—reformate (C5+), hydrogen, BTX aromatics, and LPG—are highly dependent on several interacting factors:

- **Feedstock Composition:** Naphthas rich in naphthenes and aromatics precursors will generally yield more aromatics and hydrogen. Paraffin-rich naphthas will yield less hydrogen and may produce more light ends if processed at high severity.
- **Process Technology:** CCR units, operating at lower pressures, generally achieve higher C5+ reformate yields and hydrogen yields compared to older SRR units operating at higher pressures.
- **Catalyst Type and Formulation:** Modern bimetallic or multimetallic catalysts (e.g., $Pt\text{-}Re/Al_2O_3$, $Pt\text{-}Sn/Al_2O_3$) are designed for improved selectivity towards desired products and better stability, influencing overall yields. For example, UOP's R-264 catalyst is reported to offer C5+ yield advantages.
- **Operating Severity:** This is a key operational variable, primarily controlled by reactor temperature.
    - **Low Severity:** Results in lower octane reformate, higher C5+ yield, lower aromatics yield, and lower hydrogen production. Coke make is generally lower, allowing for longer catalyst cycle lengths in SRR units.
    - **High Severity:** Produces higher octane reformate, higher aromatics yield, and typically higher hydrogen yield (up to a point, beyond which excessive cracking might reduce it). However, C5+ liquid yield tends to decrease due to increased hydrocracking, leading to more LPG and fuel gas production. Coke make is also higher, requiring more frequent regeneration or higher regeneration capacity in CCR units. A specialized patent describes a process involving specific hydrocracking and recycle steps to target particular LPG and BTX yields. Optimizing product yields is a complex task requiring a careful balance of these factors. Refineries often use sophisticated process models to determine the most economical operating point based on current feedstock costs, product values, and operational constraints. There is often a trade-off between maximizing reformate octane or aromatics production and maximizing overall C5+ liquid yield, as well as balancing reformate yield with hydrogen production to meet the refinery's internal demands.

Table 5.1: Illustrative Product Yields for Different Platforming Technologies and Severities (Approximate Ranges)

Feedstock Type / Technology / Severity	Reformate (C5+) (vol% on feed)	Hydrogen (wt% on feed)	Total Aromatics in Reformate (wt%)	LPG (C3+C4) (wt% on feed)
Rich Naphtha (High Naphthene)				
SRR - Moderate Severity	80-88	1.5-2.5	50-65	5-10
CCR - High Severity (Max Octane)	78-85	2.5-3.5	65-75	8-15
CCR - Max Aromatics Mode (e.g., for BTX)	75-82	3.0-4.0	70-80+	10-18
Lean Naphtha (High Paraffin)				
SRR - Moderate Severity	75-83	1.0-2.0	40-55	8-15
CCR - High Severity (Max Octane)	72-80	1.8-2.8	55-70	12-20
Note: These are generalized, illustrative ranges. Actual yields vary significantly based on specific feedstock properties, catalyst type, precise operating conditions, and unit design. Data synthesized from principles discussed in.				

This table provides a conceptual overview of how product distribution can shift based on the feedstock, the chosen reforming technology, and the operational strategy (severity). It underscores the flexibility of the platforming process but also the complex interplay of variables that refiners must manage to optimize their output according to market demands and economic objectives.

6. Worldwide Survey of Platforming

The platforming process is a globally ubiquitous technology in petroleum refining, with continuous advancements in catalysts, process design, and operational practices driven by major technology licensors and the evolving demands of the energy and petrochemical markets.

6.1. Global Catalytic Reforming Capacity and Trends

Catalytic reforming is a cornerstone process in refineries worldwide. As of 2023, OPEC estimated global catalytic reforming capacity additions between 2023 and 2045 to be significant, with 1.17 million barrels per day (mb/d) of existing projects and a further 1.6 mb/d of new unit additions anticipated in the medium term (2023-2028). The long-term additions (up to 2045) are projected at 19.2 mb/d for overall refining capacity, with catalytic reforming being a key component of these expansions, particularly in developing regions like Asia-Pacific, the Middle East, and Africa, mirroring shifts in regional demand. For instance, in China, major oil companies like PetroChina and Sinopec Corp. had catalytic reforming capacity ratios to atmospheric distillation capacity around 7.7% and 8.2%, respectively, as of an earlier report, indicating substantial existing capacity. The U.S. Energy Information Administration (EIA) tracks overall U.S. refinery capacity, which stood at 18.1 million bbl/cd at the start of 2023, with catalytic reforming units being integral to these facilities. The demand for reforming catalysts is projected to grow, with some estimates suggesting the overall refinery catalyst market, which includes reforming catalysts, could reach $6.8 billion by 2029, growing at a CAGR of around 4%. This growth is driven by the need for clean fuels and petrochemical feedstocks.

A significant trend in the global adoption of platforming technologies is the sustained shift from older Semi-Regenerative (SR) units towards Continuous Catalyst Regeneration (CCR) technology. While SR catalysts still accounted for over one-third of total catalyst demand as of a 2021 report, a 10+ year trend shows increasing demand for CCR catalysts and declining demand for SR catalysts, a trend expected to continue. This shift is primarily due to the superior yields, higher on-stream factors, and greater operational flexibility offered by CCR units, which operate at lower pressures and higher severities. Most new reforming units being built are of the CCR design.

The drive towards crude-to-chemicals projects, where refineries are increasingly configured to maximize petrochemical output rather than just transportation fuels, is another major trend impacting reforming. Catalytic reforming is a primary technology for producing aromatics (BTX), which are key petrochemical building blocks. This trend will likely sustain demand for reforming capacity, particularly for technologies optimized for aromatics production, such as Axens' Aromizing™ process or UOP's aromatics-focused CCR operations.

6.2. Market Trends for Different Platforming Technologies (CCR vs. SR)

The market for platforming catalysts and technologies clearly favors CCR systems. The projected annual growth in reforming catalyst consumption is almost twice that for heavy naphtha itself, indicating an increasing intensity of catalyst use, likely driven by the more demanding operations and catalyst cycling in CCR units. The economic advantages of CCR technology, including higher C5+ reformate and hydrogen yields, higher achievable octane, and continuous operation, generally outweigh the higher initial capital cost for new constructions and major expansions. This is particularly true for larger refineries where economies of scale are significant. However, SR technology still holds a portion of the market, especially for smaller refineries or in regions where capital constraints are more severe. Catalyst manufacturers continue to supply both SR and CCR catalysts to cater to the existing diverse global installed base. Some licensors also offer revamp options to convert existing SR units to CCR-type operations or hybrid SR/CCR units, providing a phased investment pathway to improved performance.

6.3. Recent Advancements and Innovations in Platforming Technology and Catalysts

Technology licensors and catalyst manufacturers are continuously innovating to improve the efficiency, selectivity, and environmental performance of platforming units.

- **Catalyst Developments:**
    - **UOP:** Has introduced advanced CCR catalysts like the R-260 series (e.g., R-262, R-264) which offer higher density, tailored pore structures, and re-optimized metal/acid balance compared to older series like R-130. These catalysts aim to increase throughput and/or yields while reducing coke production. The R-264 catalyst, for example, is designed for maximum yield or maximum activity modes and shows significantly lower coke make than previous generations. UOP's R-262 catalyst is specifically designed for CCR units operating under severe conditions or with higher sulfur in the feed, containing a higher platinum level to maintain metal function.
    - **Axens:** Offers the Symphony® family of catalysts for both CCR (Pt/Sn based, e.g., PS 100, PS 110, CR 157 for gasoline; AR 151 for aromatics) and Semi-Regenerative/Cyclic units (Pt/Re based, e.g., PR 150, PR 156, RG 682, PR 250, PR 256). These catalysts are multipromoted and designed for high selectivity, activity, stability, and improved regeneration characteristics (e.g., better Pt redispersion, chloride retention). Axens continuously works on catalyst development, as highlighted by technical articles on "Development in reforming catalysts: a never ending story". They launched the P/PR 200 series in the Symphony® family in 2021.
    - **General Trends:** Research focuses on enhancing metal-support interactions, optimizing promoter effects (Re, Sn, Ir), improving resistance to coke and poisons, and achieving better metal dispersion and stability through advanced preparation techniques and support materials. The use of mesoporous zeolites and other novel support materials is being explored to enhance catalyst performance.
- **Process Design and Operation:**
    - **Regeneration Systems:** UOP's CycleMax™ regenerator and Axens' RegenC-2™ are examples of advanced regeneration systems designed for efficient coke burn-off, optimal metal redispersion, and minimal catalyst damage, contributing to longer catalyst life and stable performance.
    - **Reactor Internals and Flow Dynamics:** Improvements in reactor design, such as UOP's upflow centerpipe and optimized scallops, aim for better vapor distribution and catalyst utilization, as well as reduced catalyst attrition. Axens also emphasizes optimized side-by-side reactor arrangements.
    - **Digitalization and Process Control:** Advanced process control, online monitoring (e.g., for oxygen and moisture in regeneration), and the use of digital tools (digital twins, AI/ML models) are being increasingly adopted to optimize reactor performance, predict maintenance needs, and enhance safety and reliability.
    - **Feedstock Flexibility:** There is ongoing work to enable reformers to handle a wider range of feedstocks, including those derived from unconventional sources or co-processing of bio-feeds or pyrolysis oils, although this presents significant

challenges due to impurities. For instance, processing pyoil-derived naphtha in CRUs requires careful assessment of silicon and nitrogen content due to high catalyst sensitivity.

- **Kinetic Modeling:** Fundamental kinetic models, like that by Sotelo-Boyas and Froment for Pt-Sn/Al_2O_3 catalysts, continue to be refined. These models provide deeper insights into reaction mechanisms and are crucial for catalyst design and process optimization.

6.4. Impact of Environmental Regulations

Environmental regulations have a profound impact on the design, operation, and evolution of catalytic reforming technology. The primary drivers are the need for cleaner transportation fuels with reduced harmful emissions.

- **Benzene Reduction:** Benzene is a known carcinogen, and its content in gasoline is strictly regulated in many countries. Since reformate is a major contributor to benzene in the gasoline pool, refiners must implement strategies to limit it. These include:
    - Modifying reformer feed by prefractionation to remove benzene precursors (cyclohexane, methylcyclopentane).
    - Post-fractionation of reformate to separate a benzene-rich cut, which can then be processed further (e.g., extraction for chemical use, or saturation to cyclohexane).
    - Operating the reformer at conditions that minimize benzene formation, although this can be challenging without sacrificing octane. This regulatory pressure has spurred innovations in benzene management technologies and influences the economic viability of aromatics extraction versus other benzene reduction routes.
- **Sulfur Reduction (Impact on Hydrogen Demand):** Regulations mandating ultra-low sulfur gasoline and diesel (ULSD) have significantly increased the demand for hydrogen in refineries for hydrotreating processes. Catalytic reformers are a primary source of this hydrogen. Thus, the need for more hydrogen often drives decisions to improve reformer efficiency, increase severity (if hydrogen yield benefits), or even install new reforming capacity. The value of hydrogen as a byproduct has become a more significant factor in reformer economics.
- **Overall Aromatics Content and Olefins:** Some regulations also aim to limit total aromatics or olefins in gasoline due to their potential to form ozone or other pollutants. While reformate is high in aromatics (which are good for octane), this can create blending challenges if total aromatics limits are very strict. This may lead to strategies that favor isoparaffin production over aromatics or require blending with lower-aromatic, high-octane components like alkylate.
- **Greenhouse Gas (GHG) Emissions:** The energy-intensive nature of reforming (due to endothermic reactions and fired heaters) contributes to refinery GHG emissions. Efforts to improve energy efficiency, such as enhanced heat integration, more efficient furnaces , and catalyst developments that allow operation at lower temperatures or severities for a given octane target, are indirectly driven by the broader goal of reducing carbon footprints.

In response to these regulations, technology licensors are developing solutions that help refiners meet stricter fuel specifications while maintaining profitability. This includes catalysts that offer higher selectivity to desired products (thus reducing unwanted byproducts that may be regulated), processes that maximize hydrogen yield, and integrated solutions for benzene and aromatics management. The trend towards "cleaner fuels" is a continuous driver for innovation in catalytic reforming.

7. Conclusion

Platforming, or catalytic reforming, stands as a cornerstone technology in the petroleum refining industry. Its multifaceted role in producing high-octane gasoline blending components, valuable aromatic feedstocks for the petrochemical sector (BTX), and substantial quantities of hydrogen crucial for refinery-wide clean fuel production underscores its enduring significance. The evolution of platforming from early non-regenerative units to sophisticated Continuous Catalyst Regeneration (CCR) systems highlights a relentless pursuit of efficiency, yield optimization, and operational flexibility, driven by market demands and increasingly stringent environmental regulations.

The fundamental chemistry of platforming, involving a complex interplay of dehydrogenation, dehydrocyclization, isomerization, and controlled hydrocracking reactions, is facilitated by advanced bifunctional catalysts. These catalysts, typically comprising platinum and promoters like rhenium or tin on a chlorinated alumina support, are meticulously designed to balance metal and acid functions, thereby maximizing desired product yields while minimizing deactivation through coking, poisoning, and sintering. The continuous innovation in catalyst formulation and regeneration techniques, particularly within CCR technology, allows for operation at lower pressures and higher severities, unlocking superior product quality and economic benefits. Leading technology licensors such as Honeywell UOP and Axens have been at the forefront of these advancements, offering proprietary CCR processes, catalyst families (e.g., UOP's R-series, Axens' Symphony® series), and highly efficient regeneration systems (e.g., CycleMax™, RegenC-2™). While CCR technology dominates the market for new units and major revamps due to its inherent advantages, older technologies like Semi-Regenerative Reforming still find application, particularly in smaller refineries.

The products of platforming—high-octane reformate, BTX aromatics, hydrogen, and LPG—are all vital to the modern economy. However, their production must be managed in the context of environmental stewardship, particularly concerning benzene emissions and the overall drive for cleaner fuels. This has spurred further innovation in feedstock preparation, benzene management strategies, and technologies that enhance hydrogen production to support desulfurization efforts.

Looking ahead, the platforming process will continue to adapt. The global trend towards crude-to-chemicals will likely increase the emphasis on maximizing aromatics production. Simultaneously, the demand for high-quality, clean transportation fuels will necessitate ongoing improvements in catalyst performance and process efficiency. As the refining industry navigates the complexities of the energy transition, the strategic importance of platforming, with its ability to upgrade low-value naphtha into multiple high-value streams, is set to remain undiminished. Future developments will likely focus on further enhancing catalyst robustness, improving energy efficiency, and potentially integrating platforming with emerging technologies for processing renewable or circular feedstocks, ensuring its continued relevance in a changing energy landscape.

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