PROCESSES TO IMPROVE THE QUALITIES OF DISTILLATES
4.1.1 Introduction

UOP (Universal Oil Products) designed the first catalytic reforming unit in 1949, the Platforming process, in which naphtha feedstock is processed over a platinum-containing catalyst to produce reformate and hydrogen. Reformate is a high octane number blending component used in the production of gasoline, with a high aromatic content. It is commonly used also as a feedstock to an aromatics complex producing benzene, toluene and xylene. The feed should be previously hydrotreated as to avoid poisoning of the catalyst.

The first Platforming units were designed as semi-regenerative (SR), fixed-bed units employing monometallic catalysts comprised of platinum on an alumina support. Fixed-bed units had to be periodically shutdown to regenerate the catalyst, including burning off coke deposits and reconditioning the catalyst’s active metals. To maximize the length of time (cycle) between regenerations, these early units were operated at high pressures in the range of 2,750 to 3,450 kPa (400 to 500 lb/in² gauge).

UOP initially improved the Platforming process by introducing bimetallic catalysts to SR Platforming units. These catalysts enabled a lower-pressure, higher-severity operation: pressure in the range of 1,350 to 2,100 kPa (195 to 305 lb/in² gauge), reformate with 95 to 98 octane number and typical cycle lengths of one year. The increased rate of catalyst coking at the higher severity limited the operating run length and the ability to further reduce pressure. Cyclic reforming was developed during the 1960s to sidestep this barrier. It employs fixed-bed reforming, but the reactors can be individually taken off-line, regenerated, and then put back into service without shutting down the unit and losing production.

UOP commercialized Platforming with continuous regeneration in 1971 with the CCR (Continuous Catalyst Regeneration) Platforming process. The process employs continuous catalyst regeneration by means of a moving-bed technology; catalyst is continually removed from the last reactor, regenerated in a controlled environment, and then transferred back to the first reactor. The CCR Platforming process represents a step change in reforming technology. With continuous regeneration, coke laydown is no longer a barrier to operating severity because the coke is continuously burned off and the catalyst is reconditioned to its original performance.

The process has enabled ultra-low pressure operations at 345 kPa (50 lb/in² gauge), which result in the highest liquid yield and produced product octane number levels as high as 108.

The continuous regeneration approach has been very successful commercially with more than 95% of new catalytic reformers being designed as CCR Platforming units. In addition, many units that were originally built as SR Platforming units have been revamped to CCR Platforming units.

4.1.2 General process description

In a typical reforming scheme (Fig. 1), hydrotreated naphtha feed is combined with recycled hydrogen gas and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and
sent to the reactor section. Typically three or four adiabatic, radial flow reactors are arranged side-by-side. The predominant reactions are endothermic, thus an interheater is used between each reactor to reheat the charge to reaction temperature. Waste heat in the flue gas from the fired heaters is typically used to generate high pressure steam, though other heat integration options are available.

The effluent from the last reactor is heat exchanged against combined feed, cooled and split into vapour and liquid products in a separator. The vapour phase is rich in hydrogen gas. A portion of the gas is compressed and recycled back to the reactors. The net hydrogen-rich gas can be compressed and combined with the separator liquid phase at higher pressure and/or lower temperature for additional liquid product recovery. This recovery section can be engineered and optimized to provide the required performance. The liquid product from the recovery section is sent to a stabilizer where light saturates are removed from the aromatics-rich reformate product.

**4.1.3 Process chemistry and catalysts**

The Platforming process produces aromatics from naphthenes and paraffins, either for use in motor fuel or as a source of specific aromatic compounds while minimizing ring opening or cracking. In aromatics applications, the feed naphtha is generally restricted to C₆ through C₈ compounds to maximize the production of benzene, toluene, and xylenes. The distribution of the hydrocarbon types (paraffins, naphthenes and aromatics) will determine how easily various naphthas can be reformed. Aromatic compounds pass through the reforming unit relatively unchanged; naphthenes react rapidly and efficiently to aromatics, while paraffins react slowly and with less selectivity.

A generalized reaction scheme that identifies these key reactions, as well as the reaction pathways that are required to achieve high product yields, is depicted in Fig. 2. Two key catalyst functions are served by acid and metal sites. Three major reactions shown in Fig. 3, dehydrocyclization, isomerization, and dehydrogenation, occur in a reforming unit to produce the desired products. Reactions such as hydrocracking and dealkylation (Fig. 4) are undesirable.

Great advances have been made over the past two decades combining improved catalyst formulations with lower operating pressures that better product yields for the key reactions. Catalyst system performance, as measured by activity and selectivity to desired reactions, is achieved by the balance between acid and metal sites.

Most catalysts contain platinum and chloride supported on alumina, providing the metal and acid functions, respectively. Early reforming units used fixed-bed catalyst systems and the catalysts contained only platinum for the metal function. These catalysts produced high octane number product, but they quickly deactivated by coking the active sites on the catalyst. Due to rapid deactivation, high operating pressures were used to minimize the coke lay down. There have been great advances improving fixed-bed catalyst formulations over the years.

Now these catalysts may be bimetallic or trimetallic with customization of catalyst system performance. The advent of bimetallic catalysts in the 1960s, containing both...
platinum and rhenium, resulted in catalysts that were more stable, less susceptible to coke formation, and could be operated at more severe conditions. Since the introduction of bimetallic catalyst, formulations have continued to improve allowing more severe operating conditions and resulting in higher octane number and more reformate product.

As mentioned earlier, continuous reforming was introduced in the early 1970s with the commercialization of the UOP CCR Platforming process. The CCR Platforming process overcame operating limits caused by rapid catalyst deactivation. Catalyst formulations quickly evolved to take advantage of this capability and enabled operation at conditions resulting in the highest yields of hydrogen and high-octane number gasoline, as shown in Fig. 5 where the liquid reformate (naphtha) yields are correlated to the unleaded Research Octane Number (RON).

4.1.4 Process variables

Process variables that may be adjusted by design or during operation include: reactor temperature, pressure and space velocity, hydrogen / hydrocarbon ratio, and feedstock characteristics. The relationships of the variables generally apply to both fixed-bed reforming and continuous reforming.
Reactor temperature. Once a process unit has been installed, the primary mechanism to adjust product octane number is that of adjusting reactor operating temperatures. Typical reactor inlet temperatures range from 490°C to 550°C. With the other operating conditions held constant, a higher reactor inlet temperature results in a higher product octane number. Higher temperatures also increase operating severity and cause more rapid catalyst deactivation.

Reactor pressure. reactor operating pressure can practically vary from 3.5 to 30 bar, although there are no theoretical limits. As a consequence of the typical catalyst distribution between the reactors, the last reactor inlet pressure provides a close approximation of the average pressure in the overall catalyst bed. The lower the operating pressure, the higher the reformate and H₂ yields. Low operating pressure results in more severe conditions, causing higher catalyst deactivation rates. The lowest operating pressures are typically only practised in continuous reforming units.

Space velocity. Space velocity is the ratio of the feed rate to the amount of catalyst. It is typically measured in volumetric terms as Liquid Hourly Space Velocity (LHSV) in units of h⁻¹. Space velocity affects the temperature required to achieve a desired product quality. Lower space velocity entails larger catalyst volumes, signifying that lower temperatures are required to achieve the same product quality. High space velocity, a more severe condition, results in higher temperature requirements for the same product quality. Following the construction of a reforming unit, the LHSV can only be adjusted by varying the naphtha charge rate.

Hydrogen/hydrocarbon ratio. The hydrogen/hydrocarbon ratio, or H₂/HC, is the measure of moles of hydrogen charged to the reactor as a ratio of the moles of feed naphtha. As mentioned earlier, hydrogen is recycled to the reactors to maintain catalyst stability. The amount of the hydrogen or H₂/HC can be adjusted by the rate of recycled gas at a given operating pressure. The hydrogen purity of the separator gas also has a direct effect on H₂/HC. A higher H₂/HC results in a less severe operation and thus a lower catalyst deactivation rate. Operation at higher H₂/HC must be balanced with the utility cost associated with recycling the separator gas.

Feedstock. Feedstock can be characterized by the relative proportions of paraffins, naphthenes and aromatics (PNA) in the feed along with its distillation range. The fastest reactions are those of naphthenes dehydrogenation. Feedstocks rich in naphthenes require less severe conditions to reach a product octane number target or aromatic concentration. Feedstocks that are lean in naphthenes and correspondingly higher in paraffins require more severe operating conditions to obtain a specific quality product. A feedstock with a wide boiling range or one with a higher end point will also require more severe conditions to reach product targets. When reformate is produced for the purpose of feeding an aromatics complex, the boiling range of the feedstock tends to be more narrow, limited to the range that results in the desired aromatic species.

4.1.5 Industrial technologies

Semi-regenerative reforming

As the catalyst deactivates in fixed-bed reforming, the reactor inlet temperatures are gradually increased to maintain product octane number.

Semi-regenerative reforming is the original method of management of deactivation, introduced by UOP in 1949. UOP’s RZ Platforming process is another fixed-bed system that uses semi-regenerative reforming technology. The RZ Platforming process is described in more detail below.

In a typical semi-regenerative reforming unit, treated naphtha feed is combined with recycled hydrogen gas and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and sent
to the reactor section. Down-flow or radial-flow reactors are arranged in a conventional side-by-side pattern.

The catalyst deactivates over time at reaction conditions. Typical cycle lengths range from six to twenty-four months. Generally, in-situ catalyst regeneration for rejuvenation of the catalyst is conducted. After the catalyst has deactivated to the point where the desired product can no longer be achieved, the unit is taken off-line, the reactors are purged of hydrocarbons and the catalyst is regenerated. Regeneration employs a low concentration oxygen environment that burns the coke from the catalyst. The unit can then be placed back on stream with near new catalyst performance. Over the course of many years and regeneration cycles, the catalyst will lose the ability to be rejuvenated to nearly new performance and it is replaced.

**Cyclic regenerative reforming**

Cyclic regenerative reforming is an extension of the semi-regenerative paradigm. In cyclic reforming, fixed-bed reactors swing in and out of reforming service and are regenerated individually. This allows for nearly continuous operation of the reforming unit. Typically, there are five or six reactors and large valves permit the removal of any reactor from the process for regeneration. Cyclic operation allows higher severity (hence, higher RON) than semi-regenerative reforming. The regeneration is often suboptimal.

**Continuous reforming**

The CCR Platforming process uses moving-bed units that operate at more severe conditions than fixed-bed reforming units, specifically at lower pressure, to maximize liquid yield (Fig. 6). In the years since the start-up of the first unit, UOP has continued to improve and expand regeneration capability to keep the CCR regenerator system in balance with the requirements of the reactor section. A continuous catalyst regeneration system (octanizing process) was also developed by IFP (Institut Français du Pétrole, now Axens).

Continuous catalyst regeneration is a complete departure from the semi-regenerative paradigm, in that operation and performance are constant and smooth. Radial-flow reactors are arranged in a vertical stack for CCR Platforming units (Fig. 7). Catalyst flows vertically by gravity down the stack, while the charge flows radially across the anular catalyst beds. Over time, coke builds up on the Platforming catalyst at reaction conditions. Partially deactivated catalyst is continually withdrawn from the bottom of the reactor stack and transferred to the CCR regenerator. The catalyst flows down through the regenerator where the accumulated carbon is burned off and the moisture and chloride levels are adjusted. Regenerated catalyst is lifted with hydrogen to the top of the reactor stack. Since the reactor and regenerator sections are separate, each can operate at its own optimum conditions.

In addition, the regenerator section can be temporarily shut down for maintenance without affecting the operation of the reactor and the product recovery sections.

Regeneration sections are tailored to provide fresh condition catalyst to the reactors. Each step is optimized. Typical advantages of continuous reforming technology include: a) high utilization of feed due to low operating pressure; b) on stream factor of more than 95%; c) flexibility to process a wide variety of feedstock; d) only two catalyst lifts for minimal catalyst attrition; e) stacked reactors for economical design; f) optimized heat and compression integration for every unit; and g) liquid recovery optimized on every unit.

One of the key factors in maintaining catalyst performance (particularly, constant reformate and hydrogen yields) throughout catalyst life is the ability of the CCR regenerator to completely regenerate the catalyst. Features of the CCR...
regenerator include: a) an elegant design that rejuvenates spent catalyst to fresh-like conditions while maximizing catalyst life; b) a safe transition between hydrocarbon and oxygen-containing equipment that is automatically assured by UOP’s reliable catalyst regeneration control system; c) valveless control of catalyst flow that is extremely reliable without the maintenance costs of expensive control valves; d) operability and reliability that has steadily increased through years of improvement.

RZ Platforming

UOP’s RZ Platforming process is a fixed-bed system that is well suited for use in aromatics production facilities, particularly for those producers requiring large amounts of benzene. The RZ Platforming process uses the RZ-100 catalyst. By virtue of its ability to convert the most difficult feed components (C₆ and C₇ paraffins) to aromatics, the RZ-100 catalyst represents a major step beyond conventional reforming catalyst technology. Although RZ-100 catalyst is similar in many ways to conventional reforming catalysts, it differs greatly in the production of light aromatics (benzene and toluene).

The selectivity of conventional reforming catalysts for benzene and toluene is significantly lower than for the C₆ aromatics. By comparison, the selectivity of the RZ-100 catalyst for light aromatics is vastly improved. This improved selectivity can be illustrated by comparing its aromatics selectivity to that of conventional low-pressure CCR Platforming catalyst. The RZ Platforming process is primarily used for situations in which higher yields of BT aromatics and hydrogen are desired.

Although the continuous reforming process is the most efficient means possible for producing xylenes from heavier naphtha fractions, its conversion of C₆ and C₇ paraffins to aromatics is normally below 50%, even at low pressure. The RZ Platforming process offers constant aromatics selectivity, in the range of 80% or higher, even when processing the most difficult C₆ and C₇ paraffin feed components.

Illustrations of the improved selectivity of the RZ-100 catalyst for aromatics production and increased hydrogen yield are shown in Fig. 8 and Fig. 9. The RZ-100 catalyst was compared with CCR Platforming catalyst in a controlled pilot plant test, using raffinate feed consisting primarily of C₆ and C₇ paraffins. The aromatics yields of

![Fig. 7. CCR Platforming process.](image1)

![Fig. 8. Aromatics yields from raffinate.](image2)
both catalysts were measured at the same LHSV and low operating pressure. The reactor temperature was varied to show product yields over a wide range of paraffin conversions. The higher selectivity of RZ-100 catalyst toward aromatics while processing this difficult feedstock is clearly demonstrated, ranging from 25-30 wt% higher over the span of the test.

Feedstock to the RZ Platforming unit can range from extraction unit raffinate to BTX naphtha. The RZ-100 catalyst can also be used in parallel with a conventional reforming unit to optimize the production of the desired aromatics by processing different fractions of the hydrotreated feed. In such cases, the conventional reformer can be dedicated to processing the heavier feed fraction, taking advantage of its superior ability to produce xylenes. The light naphtha, which is rich in C₆ and C₇ components, can be routed to the RZ Platforming unit, where selectivity for converting light paraffins to benzene and toluene is greatest.

**Bibliography**


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