Catalytic reforming options and practices

Design and practice in catalytic reforming is evolving to meet refinery challenges, including lower gasoline pool benzene content and increased demand for hydrogen

Tom Zhou *Fluor Enterprises*
Frederik Baars *Fluor BV*

Refiners throughout the world utilise catalytic reforming to produce high-octane reformate for gasoline blending and high-value aromatics (benzene, toluene and xylene, BTX) for petrochemical use. Reforming is also a major source of refinery-based hydrogen.

Reforming operations continue to be challenged in the context of lowering gasoline pool aromatic/benzene content; however, the catalytic reforming unit is still a mainstay of refinery operations. The recent upward trend in hydrotreatment needs has put even more emphasis on reformer hydrogen production. The main differences in technology among the various reforming processes are discussed in this article, and special attention is given to chloride control and corrosion management.

Feedstock

The standard feed to a catalytic reforming unit (CRU) is hydrotreated straight-run naphtha (SRN), typically containing C_6 through C_{11} paraffins, naphthenes and aromatics. Naphtha from different sources varies greatly in its ease of reforming. Most naphthenes react rapidly and efficiently to form aromatics. This is the basic reaction of reforming. Paraffins are the most difficult compounds to convert. A rich naphtha (lower paraffin, higher naphthene content) makes the operation much easier and more efficient. The types of naphtha used as feed to the CRU can impact the operation of the unit, activity of the catalyst and product properties. When catalytic reforming is used mainly for BTX production, a C_6-C_8 cut (initial and final boiling points IBP-FBP 60–140°C), rich in C_6, is usually employed. For production of a high-octane gasoline pool component, a C_7-C_9 cut (IBP-FBP 90–160°C) is the preferred choice.[1]

Reformate benzene content can be reduced by minimising the amount of benzene and benzene precursors (cyclohexane and methylcyclopentane) in the reformer feed via prefractionation. Alternatively, the benzene can be reduced by post-fractionation of the reformate and further processing of the light reformate.

In a refinery where maximisation of middle distillate production is a priority, the heavier portion of the naphtha that is traditionally routed to a catalytic reformer unit may instead be sent to the kerosene or diesel pool, within flash point specification limits. In most cases, a lighter CRU feed will result in an increased cycle length for a semi-regenerative (SR) unit due to decreased coke make.

Non-straight-run naphthas (for instance, fluid catalytic cracking (FCC) naphtha or visbreaker/coker naphtha) can also be processed in a CRU, but only after severe hydrotreatment involving (di)-olefin saturation, in addition to the basic naphtha hydrotreater functionality of removing heterogeneous atoms (sulphur and nitrogen). Their higher endpoint and/or higher paraffin content results in a higher coke laydown. Cyclic and continuous catalyst regeneration (CCR) reformers are generally able to process FCC naphtha with a higher feed endpoint as long as regenerator capacity exists to burn the additional coke that is produced.[2] The reprocessing of FCC naphtha is typically restricted to the lower octane middle cut. If desulphurisation only is required, processing the FCC naphtha in a selective hydrotreating unit is the more straightforward solution.

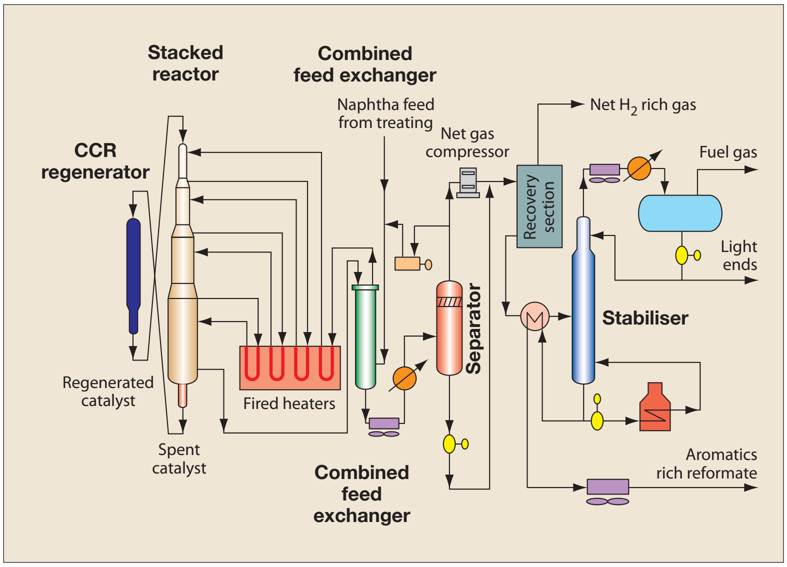

Figure 1 CCR with stacked reactors *Courtesy: UOP*

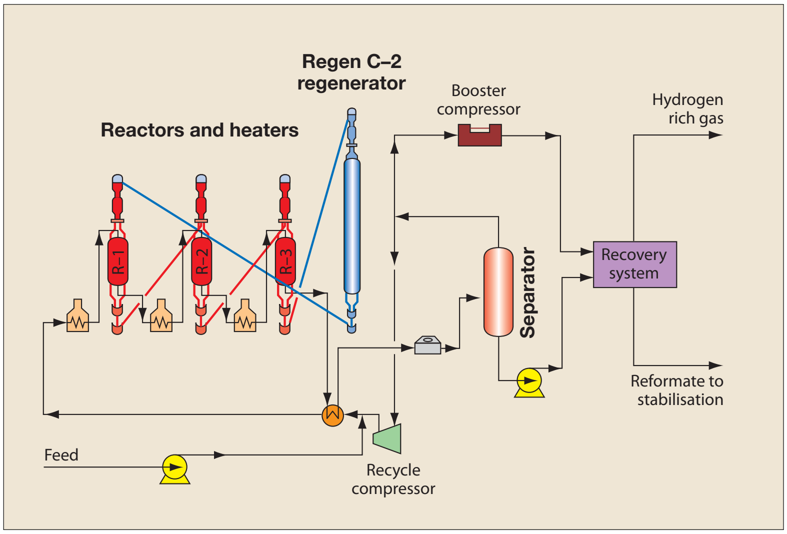

Figure 2 CCR with side-by-side reactors *Courtesy: Axens*

Fixed-bed units vs CCR reformers

The conventional CRU type is the SR fixed-bed reforming unit, which is used for limited octane improvement. The unit is operated at high pressure to mitigate carbon formation. As carbon laydown increases, reactor temperatures are raised to achieve the target octane at the expense of reformate yield. A cyclic regenerative process with a swing reactor system is used for higher severity and octane operation. With CCR reforming (see Figures 1 and 2)[3,4], extremely high severities are obtainable without frequent shutdowns due to catalyst deactivation. The units operate at a low pressure with the associated yield benefits of higher reformate and hydrogen yields.

The decision to convert high-pressure SR catalytic reformers to CCR-type units hinges entirely on economics.[5] Some reforming licensors have developed a hybrid unit, by adding a CCR reactor and regenerator to an original SR reforming unit.[4,6,7,8] Typical examples are shown in Figures 3 and 4. The conversion could cost less than half that of a new CCR and increases throughput and/or cycle length.[4]

To some refiners, a complete conversion to CCR remains economically attractive relative to a hybrid unit, due to the higher on-stream factor, lower operating pressure, and higher yields of hydrogen and naphtha.[9] Virtually all new reforming units are of the CCR design.

Reactor design

There are three types of reactors predominantly in use in the reforming process. These are spherical, downflow and radial. As catalyst improved over the years, the reactor pressure could be reduced to take advantage of the increased C_5+ and hydrogen yields at lower operating pressure. At lower pressure, the pressure drop through the reactor becomes an important consideration; therefore, more modern designs of reforming units employ reactors that are radial flow in design and combine good flow distribution with low pressure drop.

The combined feed is directed from the reactor inlet nozzle into so-called scallops, which are long, vertical channels positioned along the entire circumference of the reactor. The scallops have holes or, more commonly these days, profile wire screens along the entire length, through which gas passes radially into the annular catalyst bed and inwards to a centre pipe that collects the reactor products and directs them to the reactor outlet. Low flow should be avoided, as it will result in accelerated coke laydown.

Reactor metallurgy

Reactor vessels in a SR CRU service are standalone items and can be either hot or cold shell, depending on design preference. In cold-shell designs, an internal refractory lining protects the vessel wall from exposure to the process temperature. In CCR service, the reactors are invariably of the hot-shell design and can be either individually positioned or stacked to form a compartmented single vessel.[8] In a SR CRU, a cold wall (carbon steel with refractory lining) with an inner stainless steel liner is the norm. However, hot-shell design necessitates the use of 1.25Cr-0.5Mo, or in some cases 2.25Cr-1Mo, with stainless steel internals suitable for service above 538°C (1000°F) to meet the requirements for both high-temperature strength and resistance to hydrogen attack.

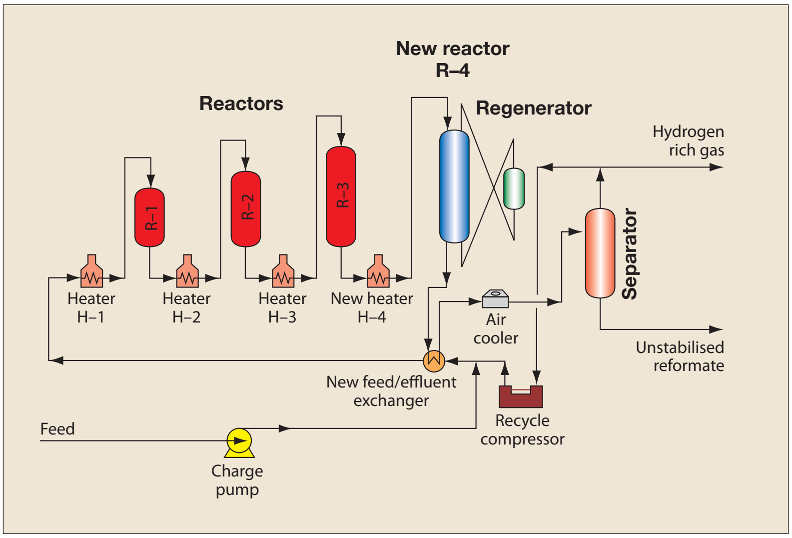

Figure 3 SR and CCR hybrid process

Courtesy: Axens

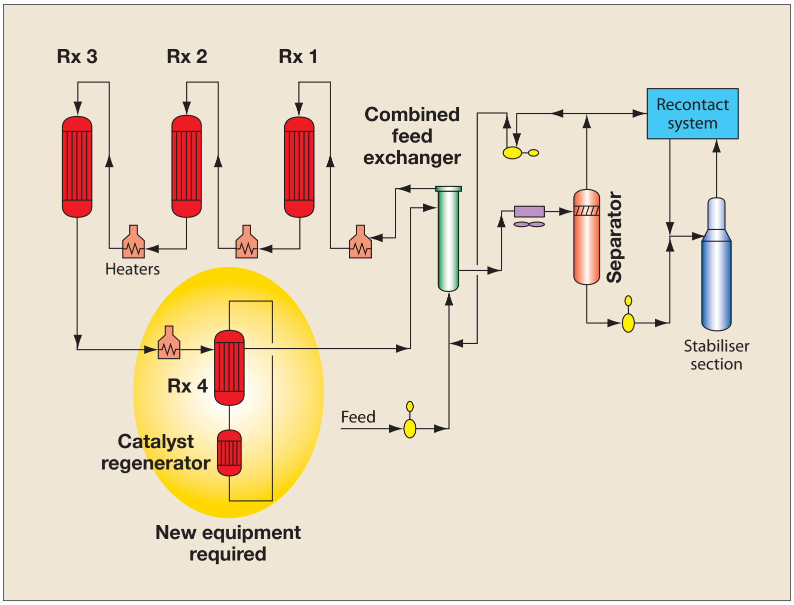

Figure 4 SR and CCR hybrid process

Courtesy: UOP

Reforming catalyst and catalyst regeneration

The reforming catalyst consists of noble metals impregnated on an alumina base, with a cylindrical (SR applications) or spherical shape (SR and CCR applications). A wide variety of metals can be used, but platinum is predominantly used. Multi-metallic catalysts composed of platinum (Pt) and rhenium (Re) are the most common type found in a fixed-bed CRU. Rhenium helps to improve catalyst life by retarding coke deposition to prevent deactivation.

Pt-Sn catalysts are utilised in CCR reforming units. The presence of tin (Sn) prevents platinum agglomeration or sintering during the regeneration and provides better Pt dispersion.[2] In the reactors, both the metal(s) and the chloride base help catalyse desirable reactions. Optimum catalyst performance requires a proper balance of these two catalytic functions. Catalyst deactivation usually occurs as a result of coke formation covering the active sites of the catalyst. To regenerate the catalyst, the coke must be burned off and the catalyst oxidised (oxychlorinated to redisperse the platinum and restore the chloride balance), dried and finally reduced. Each step of the regeneration procedure is critical to return the catalyst system to its usual high performance and to ensure long catalyst life.

SR and cyclic reformers utilise fixed-bed reforming reactor(s) for regeneration, while a CCR reformer has a dedicated moving-bed regenerator with associated piping and equipment. In SR operation, the catalyst is allowed to coke up and needs to be regenerated periodically in-situ. A cyclic reformer has a swing/spare reactor to allow unit operating severity to be maintained while one reactor is being regenerated. A cyclic or CCR reformer is more robust to feed upsets, as it is regenerated on-line. The reactor operating pressure is lower than with SR operation, which is beneficial to reformate/aromatics yield. Although the lower operating pressure accelerates coke laydown, this is taken care of by on-line regeneration.

The catalyst regeneration system in a CCR reformer performs two functions: catalyst regeneration and catalyst circulation. These days, all regeneration steps, except for reduction, occur in the regenerator. The reduction takes place in the reduction zone above the first reactor. The catalyst exits the zone and flows by gravity to the first reactor.

Catalyst developments continue, with manufacturers constantly introducing catalysts that exhibit a better yield pattern or a higher activity.

Reforming catalyst can only be regenerated if the cause of the deactivation is sulphur and/or carbon laydown. Other (permanent) sources of deactivation will typically require catalyst replacement.

Chloride-related corrosion control

To assure the metallic and acidic functions of a reforming catalyst, chloride is continuously injected into the process. Depending on the levels of nitrogen in the feed to the CRU, ammonium chloride could form and deposit on process equipment, with the risk of corrosion or reduced efficiency (for instance, in compressors). Injections with reformate, naphtha or water are an option for cleaning out salts deposited in the recycle gas compressor.[2] A good design should focus on removing organic nitrogen from the reformer feed and minimising hydrochloric acid (HCl) in the reactor loop. While the SR reformer operation is dry during normal operation, this changes during regeneration, with water being formed as a result of coke being burnt off. While the low chrome reactors are not at risk when hot during regeneration, the area downstream at the effluent cooler presents a great risk of corrosion. To maintain corrosion control during regeneration, separator water pH is kept above 7 by adjusting caustic injection during the coke burning and oxidation steps.

For CCR reforming, the regenerator and its internals are normally made of stainless steel, which is considered to be adequate for chloride corrosion resistance, since temperatures inside the regenerator are kept above the water dew point. However, special attention needs to be paid to instrument taps and nozzles, where cooling and condensation can occur. Heat tracing and nitrogen purging are required to limit chloride corrosion. Alternatively, the metallurgy can be upgraded from stainless steel to materials such as Hastelloy.

Most HCl concentrates in the reformer net gas and liquefied petroleum gas (LPG). While these streams are dry, they do not generally pose problems inside the CRU, but can create problems when mixed with other (wet) streams. Chloride absorbers (on net gas, LPG or stabiliser feed) are typically installed to overcome this.

Depending on the CCR regenerator design type, the regenerator vent gas can also contain significant amounts of HCl. Caustic scrubbers are generally employed to remove HCl from the vent gas. Recontacting the vent gas and/or reduction step purge gas with spent catalyst (aimed at reabsorbing HCl back into the process) has recently been introduced[11] as a means of reducing HCl losses and therefore chloride consumption.

References

1 Prestvik P, Moljord K, Grande K, Holmen A, *Catalytic Naphtha Reforming*, Antos G J, Aitani A M, Marcel Dekker, New York, 2004, 17–18.

2 Hydrocarbon Publishing Company, Third Quarter 2009 Hydrocracking and Catalytic Reforming, *Worldwide Refinery Processing Review*, 225–273.

3 UOP, CCR Platforming Process for Motor Fuel Production, www.uop.com/objects/CCR%20Platforming.pdf.

4 Domergue B, le Goff P-Y, Ross J, Octanizing reformer options, *PTQ*, Q1 2006, 67 & 72.

5 1996 ERTC, London, Oct 1996, Global Technology Forum, Surrey, England, 29.

6 Gendler J L, Domergue B, IFP Solutions for Revamping Catalytic Reforming Units, 1996 NPRA Annual Meeting, San Antonio, Texas.
7 Stephens G, Travers Ph, Mank L, Revamping Catalytic Reforming Units, *Revue de l'Institut du Pétrole*, 1994, 49, 5.
8 Peters S T, Platforming Technology Advances: CycleX System for Increased Hydrogen Production from a Fixed-bed Reforming Unit, 2003 NPRA Annual Meeting, San Antonio, Texas.
9 1996 NPRA Q&A and Technology Forum: Answer Book, 1996 NPRA Q&A Session, San Antonio, Texas.
10 Brear J M, Williamson J, Integrity and Life Assessment of Catalytic Reformer Units, www.seseurope.com/htm/SESpapers_pdf, SES 2006.
11 2009 ERTC UOP pre-seminar.

Fred Baars is a Technical Director with Fluor BV, Haarlem, the Netherlands, responsible for refinery studies and basic engineering projects. *Email: frederik.baars@fluor.com*

Jun (Tom) Zhou is a Principal Process Engineer with Fluor Enterprises, Houston, Texas, with experience in front-end and detailed engineering design for catalytic reforming units. *Email: tom.zhou@fluor.com*

LINKS

More articles from: Fluor

More articles from the following categories:
Catalysts & Additives
Reforming