

Octanizing reformer options

Staged investment and reformer technology improvement strategies are available for increasing hydrogen production, cycle time and reliability. Options include revamps to SR reformers and hybrid SR/CCR Dualformers, as well as new CCR unit investments

Bruno Domergue and Pierre-Yves le Goff *Axens*

Jay Ross *Axens NA*

The refining industry is investing heavily in new processing units to produce ultra-low-sulphur (ULS) fuels. As a result, hydrogen utilisation is increasing, on-stream factor and hydrogen reliability are becoming more important, and resources for other investments are scarce. Catalytic reforming is the preferred technology for producing high-octane gasoline and is usually the refinery's main source of hydrogen. Although existing reformers in North America are generally not fully utilised, many are older semi-regenerative (SR) or cyclic units with cycle times that are incompatible with continuous ULS fuels production. They produce less gasoline and hydrogen than newer ultra-low-pressure continuous catalytic regeneration (CCR) units.

CCR reforming

More than 35 Octanizing and Aromizing CCR reforming processes for gasoline- and aromatics-orientated catalytic reforming have been licensed worldwide. Ten new units were licensed in 2005. The Axens CCR reforming process is schematically represented in Figure 1, including key features for producing high-octane gasoline or aromatics-rich petrochemical streams from naphtha.

The catalyst circulation systems of these reformers are designed for long and active catalyst service as well as ease of operation and maintenance. To ensure low catalyst attrition, the lift system must be designed for continuous, smooth, non-pulsating and gentle lifting. Catalyst is continuously transferred to the regenerator, where the coked catalyst undergoes a sequence of steps involving controlled coke combustion, oxychlorination and calcination to restore the catalyst activity and metals redispersion. The proprietary RegenC-2 dry burn loop regeneration system is able to perform complete catalyst activity restoration under mild conditions to maintain catalyst activity and mechanical strength. The catalyst circulation and

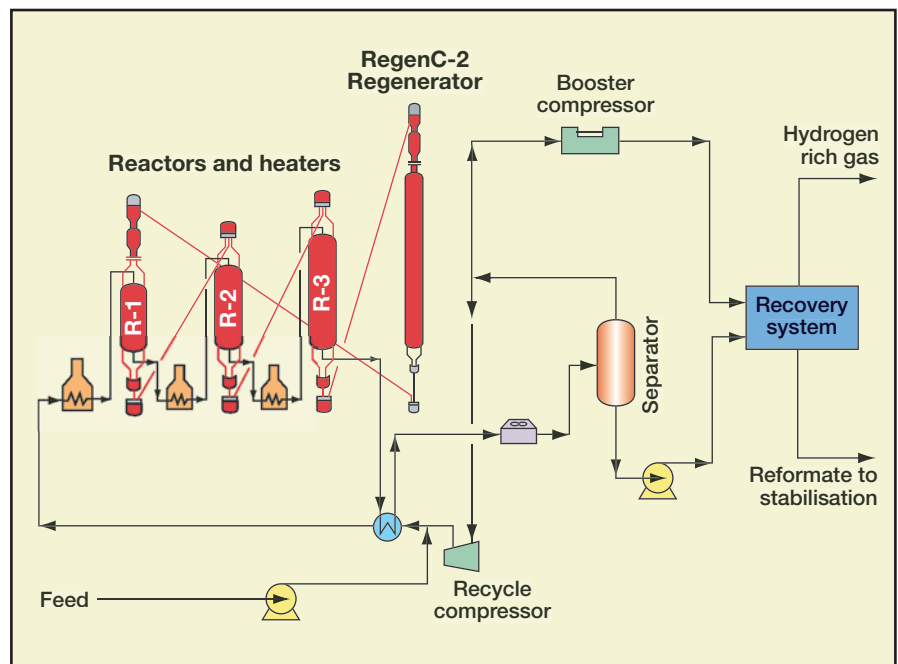


Figure 1 Axens CCR reforming process

regeneration operations are highly automated and require minimal operator attention.

The reformer's side-by-side reactor arrangement, as shown in Figure 1, has several advantages over the stacked design. Access for construction, inspection and future modifications to the reactors, as well as to the internals, is greatly increased. In addition, thermal expansion problems are minimised and the reactor structure is lighter and lower to the ground. This enables an optimal radial reactor design (L/D) without height constraints and a simplified internals structure that is less prone to mechanical problems due to thermal expansion. The reactor placement also provides for shorter catalyst transfer lines, shorter hot transfer lines between reactors and heaters, plus minimal non-flowing heel catalyst volume due to the use of spherical heads (less than 0.5% of the catalyst inventory compared to many times this in other designs). These advantages translate into significant

immediate and longer-term savings in investment, construction and maintenance costs.

The key to unit performance and long catalyst life in CCR reforming is the RegenC-2 catalyst regenerator technology. Combined with recently developed and commercialised catalysts, regenerators incorporating this technology can provide sustained catalyst performance over hundreds of regeneration cycles. Significant technology and monitoring improvements in the coke burn and catalyst oxychlorination zones result in increased catalyst life and improved operating flexibility.

RegenC-2 consists of four independent zones, depicted in the block flow diagram in Figure 2. These zones include:

- A primary burn zone equipped with a dry burn loop to minimise moisture during combustion
- A finishing zone with oxygen and temperature control (no sharp exotherms or carbon breakthrough)

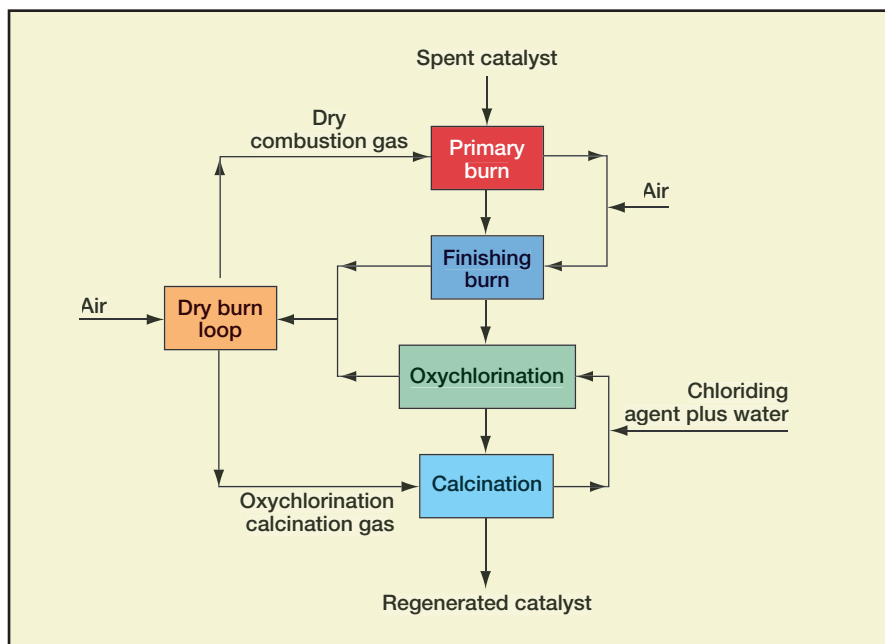


Figure 2 RegenC-2 regeneration block flow

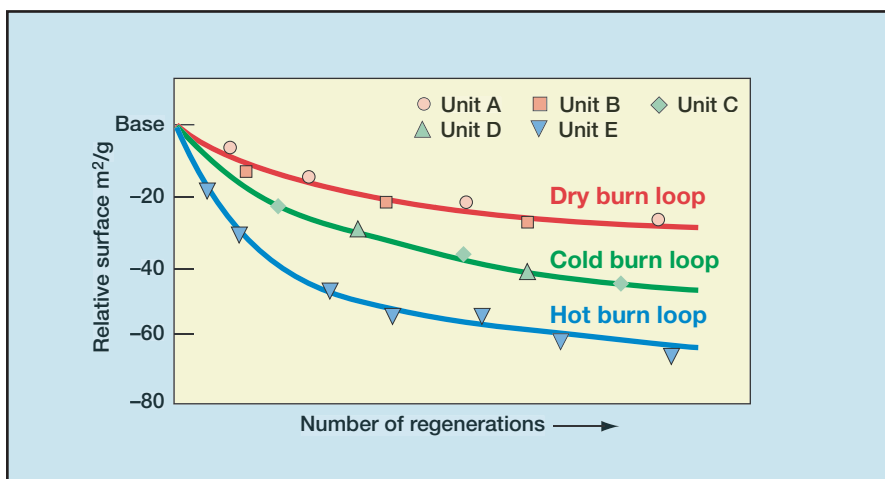


Figure 3 Surface area decline vs regeneration cycles in commercial units

- An oxychlorination zone for metals redispersion
- A calcination zone to dry the catalyst.

Coke burning is the principal function of a catalyst regeneration system. It is essential that this step be carried out to completion. However, the coke burning step is the primary contributor to three negative factors concerning catalyst performance and life:

- Metallic phase sintering, which lessens catalyst performance; in particular, stability
- Partial dechlorination of the carrier, which reduces catalytic activity
- Hydrothermal sintering of the carrier, which decreases mechanical strength and ultimate catalyst life.

The hydrothermal sintering of the alumina carrier, which occurs during regeneration and, in particular, during coke burning, results in a decrease of the specific surface area of the catalyst. The leading factors involved in carrier ageing

are the moisture level, temperature and combustion time. It is therefore critical that the water content is kept as low as possible in the combustion gases. This observation has led to the incorporation of a dry burn loop in the RegenC-2 regenerator to dry the recirculating combustion gas.

The benefits of a dry burn loop are shown in Figure 3, where catalyst surface area decay (carrier degradation) is plotted against a number of regeneration cycles for the same catalyst in three regeneration systems:

- Hot burn loop: recirculating burning gas is hot and wet
- Cold burn loop: recirculating gas is washed but not dried
- Dry burn loop: recirculating gas is washed and dried.

In normal operation, the metal dispersion is reconditioned in the oxychlorination zone. The dechlorination that occurs in the coke burning section is predominantly the result of

the moisture level in the burn zone. Accordingly, a reduction in the moisture content during combustion lowers the catalyst dechlorination, which has three advantages:

- Equipment required for chloride treatment in the combustion effluents is reduced
- Corrosion potential downstream of the combustion effluent treatment is reduced
- Chloriding agent addition during oxychlorination to compensate for the dechlorination during coke burning is reduced.

Overall, the dry burn loop RegenC-2 regenerator affords several advantages:

- Extends catalyst life: a significant increase in catalyst life compared to the hot burn loop (>900 cycles has been demonstrated)
- Reduces catalyst attrition via controlled temperature and less severe thermal cycling
- Increases catalyst stability through optimisation of the oxychlorination operating parameters throughout the catalyst life
- Improves regenerator operation flexibility due to the separation of the burn and oxychlorination gas loops
- Reduces downstream corrosion due to better chloride retention and management
- Discharges of a clean vent gas; ie, no chloride-removal equipment is required.

CCR catalysts

The CR 400/700 and AR 500 catalyst series are formulated to meet the specific needs of gasoline and aromatics production respectively. They are supplied in either a calcinated or reduced state.

The development of CR 401/AR 501 follows and anticipates the trend for high-performance ultra-low-pressure operation for new or existing units. CR 401/AR 501 have been specifically developed for reactor pressures of 3.5–7 barg (50–90psig), while for higher pressures CR 405/AR 505 are preferred. The high-performance low-density catalysts CR 701 and 702 are favoured when reduced catalyst loading is required.

The combination of catalyst properties, regenerator design and catalyst-transfer systems results in very low catalyst attrition (<2% of the inventory per year, or <0.0015% of circulation). The consequence of attrition is greater than the inconvenience and expense of catalyst addition. As fines are produced and build up in the unit, the pressure drop can increase and catalyst circulation problems can arise. In some designs, this causes a “dump and screening” of the catalyst on

a yearly or biannual basis, resulting in added downtime to remove the fines and clean the reactor screens. With the side-by-side design, fines production is minimised and on-stream time maximised.

The superior strength and stability of these catalysts has recently been demonstrated in a third-party CCR unit. After change-out to CR 702, catalyst attrition dropped by 50% (Figure 4), resulting in improved catalyst circulation and a reduction in catalyst make-up costs.

When the CR 702 catalyst was introduced into the unit, catalyst stability was also improved and the chloride addition rate was reduced by a factor of four, thereby lowering operating costs and fouling/corrosion of the downstream equipment.

Semi-regenerative reforming

In conventional semi-regenerative (SR) reforming units, many reactor designs and operating conditions vary widely from 10–30 barg (150–450psig). The older higher-pressure units exhibit relatively low reformat and hydrogen yields, while modern units, operating around 14 barg (200psig) with improved internals and catalyst systems, can provide reliable and excellent performance. Modifications to SR units, hardware and catalyst can provide substantial performance improvements. Some of the most significant changes involve the feed effluent exchangers and radial reactor performance improvements combined with a new generation of platinum-rhenium (PtRe) catalyst. These and other related modifications increase the reformer cycle length while providing incremental increases in the amount of hydrogen needed for ULS fuels production.

It is not unusual to find four, eight or even 12 feed effluent exchangers in the SR reaction section (Figure 5). This design results in a high pressure drop and poor heat transfer, limiting operation in two ways: the recycle compressor pressure drop (P) is higher and the heat duty of the first heater is higher. Replacement with a modern low pressure drop, high-efficiency welded plate exchanger can significantly increase unit throughput and decrease total pressure to improve yields.

Reactor internals

Fixed-bed radial flow reactors are used whenever a low pressure drop is critical to good performance, such as in fixed-bed reformers. It has been standard practice in radial reactor design to effectively waste the top 15% or so of the catalyst bed with a baffle arrangement to avoid reactants short-

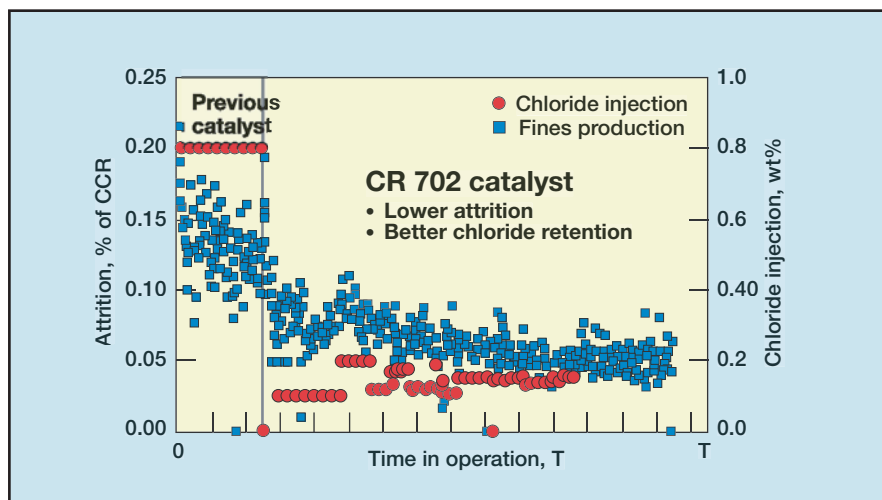


Figure 4 Reduced fines production (attrition) with CR 702

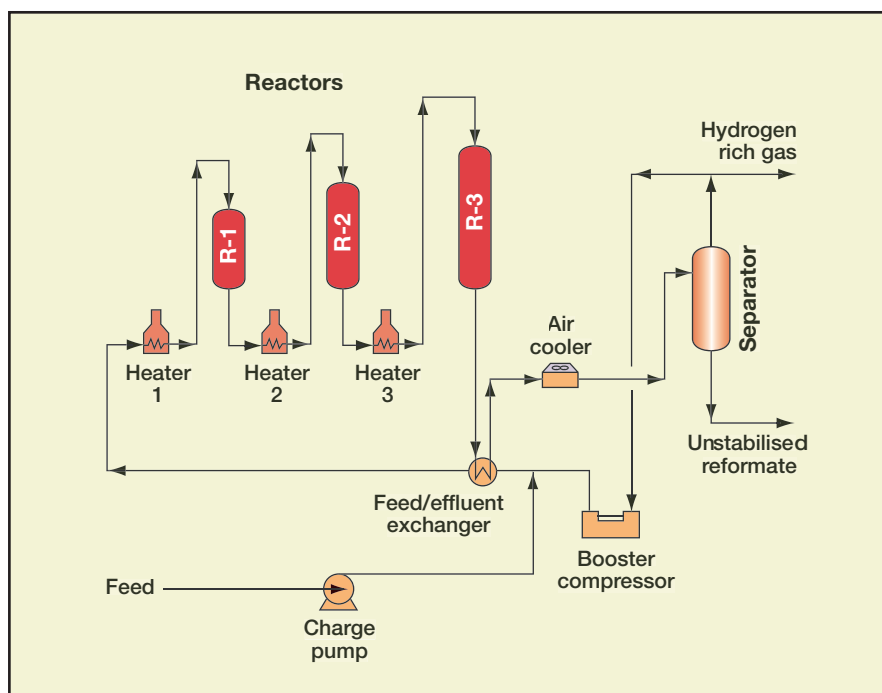


Figure 5 Semi-regenerative reformer

circuiting the bed as it settles.

Catalyst settling during the course of the run generates a gap between the top of the bed and the cover plate. Were it not for the shroud extending down into the bed, the reactants would pass preferentially through the gap (Figure 6). In addition, because of the high residence time due to poor flow dynamics in the shroud volume, the catalyst loaded at the shroud level attains higher than average coke levels. The coke found in the shroud region is difficult to burn during regeneration, so centre pipe grid damage is frequently observed in the top of the bed. Expensive reforming catalyst and reactor volume are also wasted (unused platinum inventory).

In the early 1990s, a cost-effective way to recover the unused bed volume was developed. The conventional metal

shroud was replaced with Axens' Texicap, a flexible "textile cap" flow guide that moulds to the shape of the top of the bed. This was first used in 1992 at a European refinery. The flow guide settles along with the bed, so there is no need to design dead space, and the formerly dormant catalyst section is now active. The reactor pressure drop is also reduced, as the reactants now flow through a greater catalyst bed cross-section; ie, the reactor can accept 10–15% additional feed.

Texicap is an engineered composite of refractory fibres and fillers containing no asbestos. It is impermeable and withstands the normal hydrogen/hydrocarbon atmosphere as well as the severe operating conditions of multiple regenerations encountered in reformers. Installation and removal are easy, requiring about one-tenth of the

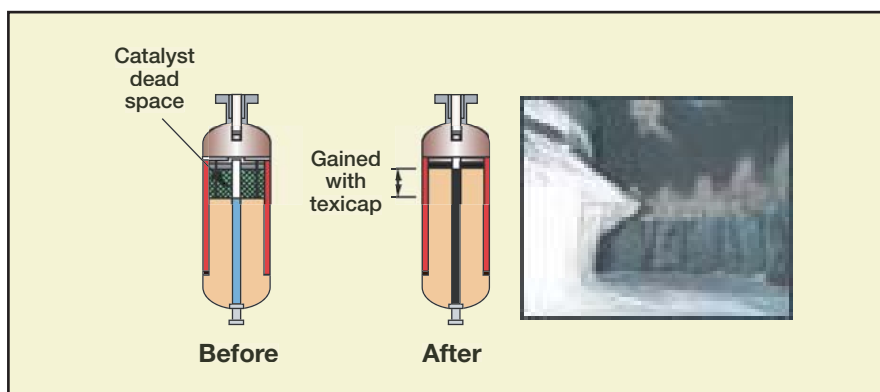


Figure 6 Texicap radial reactor installation

Investment options (10 000bpsd)				
	Case 1	Case 2	Case 3	Transform.
			Phase 1	Phase 2
Process	SR	Octanizing	SR	Octanizing
RON	96	100	96	100
Reactor pressure, barg (psig)	14 (200)	3.5 (50)	14 (200)	7 (90)
Yields, wt%				
H ₂	2.4	3.4	2.4	3.2
C ₅ +	84.3	89.1	84.3	87.9
Investment, million \$	22.2	31.8	23.5	Phase 1 + 6
Op. cost, million \$/yr	2.1	2.9	2.1	2.7
Prod. revenue, million \$/yr	11	25	11	22

Table 1

manpower and time typically needed to remove and replace a shroud and cover assembly. For a four-reactor reformer turnaround, this time can be reduced by at least 50 hours, thereby improving the on-stream time of the unit. To date, Texicap has been installed in over 70 radial reactors. Improvements have been seen in unit performance and economics due to better utilisation of the reactor volume and shorter downtime for removal and installation:

- Cycle lengths are improved at the same severity
- Severity can be increased at constant cycle length
- Platinum inventory can be reduced at same effective throughput
- Coke burning is complete and safe
- Centre pipe maintenance is reduced
- Downtime for catalyst change-out is significantly reduced.

Second-generation catalyst

RG 582 was the first commercial PtRe promoted catalyst. Providing maximum C₅+ and hydrogen yields together with excellent stability, it is used in over 70 SR and cyclic reformers. RG 682 is the latest high-performance PtRe promoted catalyst. This catalyst is designed for SR reformer applications, but can also be applied to cyclic reforming.

This optimised trimetallic catalyst features an “unbalanced” or “skewed” Re/Pt ratio (greater than one) as well as a third promoter metal. Adding

rhodium to a Pt/alumina catalyst dramatically improves stability (cycle length) by decreasing the rate of coke formation and its toxic effect on catalyst activity.

The new formulation enables excellent results to be achieved with improvements in yields, activity, stability and ease of regeneration, even at higher coke levels. The greater resistance and tolerance to coke have extended cycle life by more than 35% over that of a “conventional” balanced bimetallic Pt/Re catalyst. More than 20 loads of RG 682 are currently in operation. Commercial feedback has confirmed RG 682’s outstanding selectivity, activity, stability, regenerability and ability to recover after sulphur upsets.

The implementation of previously described unit and catalyst changes can result in extended cycle length and increased yields of reformat and hydrogen. In many cases, these modifications are able to meet the increased hydrogen requirements of new clean fuels hydrotreating units. However, cycle length may still be an issue, as ULS demands leave no room for off-spec material or lost hydrogen production during catalyst regeneration.

Semi-regenerative or CCR?

When contemplating a new project or replacing a SR reactor, consideration should be given to a staged investment

strategy. Modern SR units can provide the desired performance by using radial reactors that are designed to transform into a CCR unit at a future date when funds are available or capacity and severity requirements dictate. Providing for a future transformation requires some forethought and minimal pre-investment.

As an example, consider a reference case: 10 000bpsd feed of Middle Eastern naphtha in a reformer designed to produce 96 RON of reformate with a minimum cycle length of one year and a hydrogen delivery pressure of 21 barg (300psig). This can be accomplished in a SR unit operating at about 14 barg (200psig) or in an ultra-low-pressure CCR operating at about 3.5 barg (50psig). The CCR design also gives considerable flexibility on severity, such that a reference severity of 100 RON can be considered.

The CCR has a substantial yield advantage, but a somewhat higher cost. An alternative approach would be to consider a transformable design, whereby a SR unit is built with the ability to be converted to a CCR at a later date. These three cases are summarised in Table 1.

In the transformable case, the SR radial reactors are elevated and configured with catalyst inlet and outlet connections for the future addition of the catalyst-transfer equipment and regenerator. To optimise performance, the pressure is reduced when the unit is transformed to a CCR. The hydrogen recycle rate is also significantly lowered so that the recycle compressor can be retained, but to be able to deliver the product hydrogen at the same pressure another stage of booster compression is required. The resulting unit is almost as efficient as the ultra-low-pressure CCR (Case 2). These changes are shown in Figures 7 and 8.

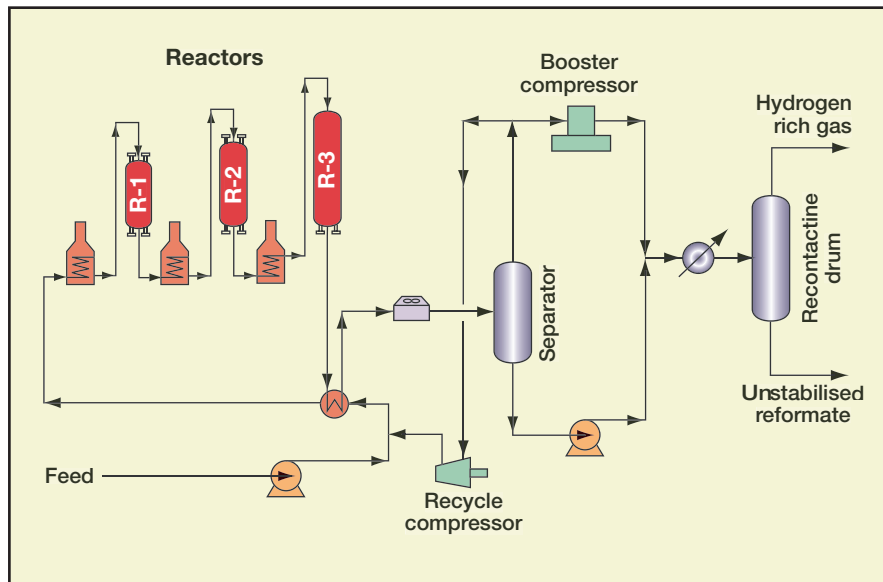


Figure 7 Phase 1 SR

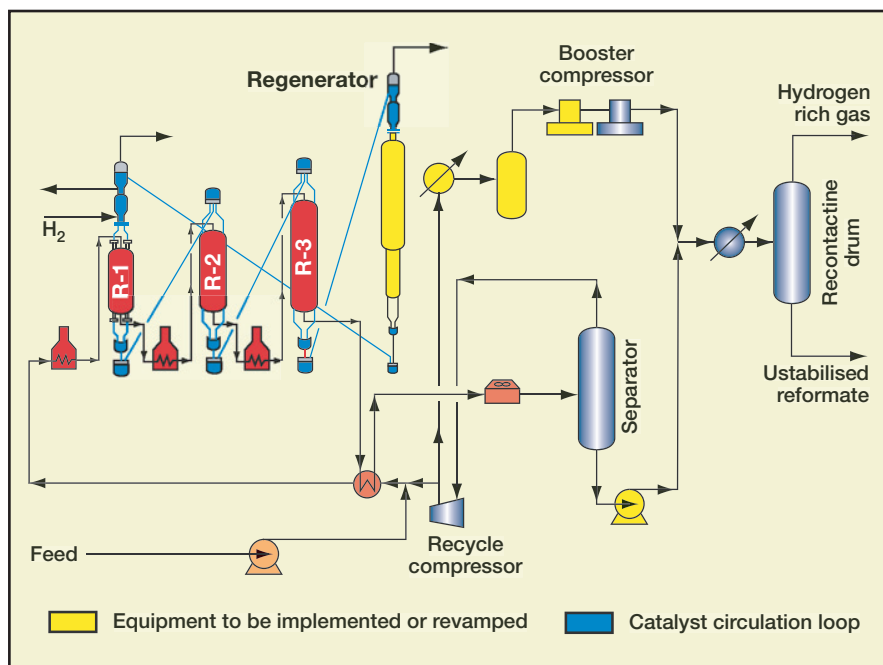


Figure 8 Phase 2 SR to CCR conversion

Commercial example

Some years ago, a refiner in southern Europe was considering a new reforming unit to help with the production of gasoline. The refinery was planning on expanding and wanted the flexibility of a future CCR unit. The unit was built as a three-reactor SR unit and operated at 98 RON and 300psig.

Several years later, the unit capacity was expanded by 50% with the addition of a fourth reactor and a slight reduction in pressure to improve yield selectivity. More recently, the need for more octane due to mandatory FCC gasoline desulphurisation presented an opportunity to implement the transformation to CCR, which was originally anticipated with a further reduction in pressure and an increase in severity to 103 RON. The

Phased construction industrial example			
	Phase 1 1979	Phase 2 1991	Phase 3 2000
Capacity, bpsd	Base	1.5 x Base	1.6 x Base
RON	98	98	103
Mode of operation	SR	SR	CCR
Number of reactors	3	4	4
Reactor pressure, barg (psig)	20 (300)	16 (240)	8 (120)
Reformate yield, wt%	79.0	80.1	78.0

Table 2

Phase 2 transformation to CCR was conducted during a scheduled refinery shutdown and required four weeks; retubing the furnaces was the limiting factor.

The sequence of unit transformation is summarised in Table 2. With a little

forethought, a unit was designed that could be expanded by over 50% with an increase in severity from 98–103 RON and minimal pre-investment. A similar strategy can be considered if existing old SR reactors require mechanical replacement.

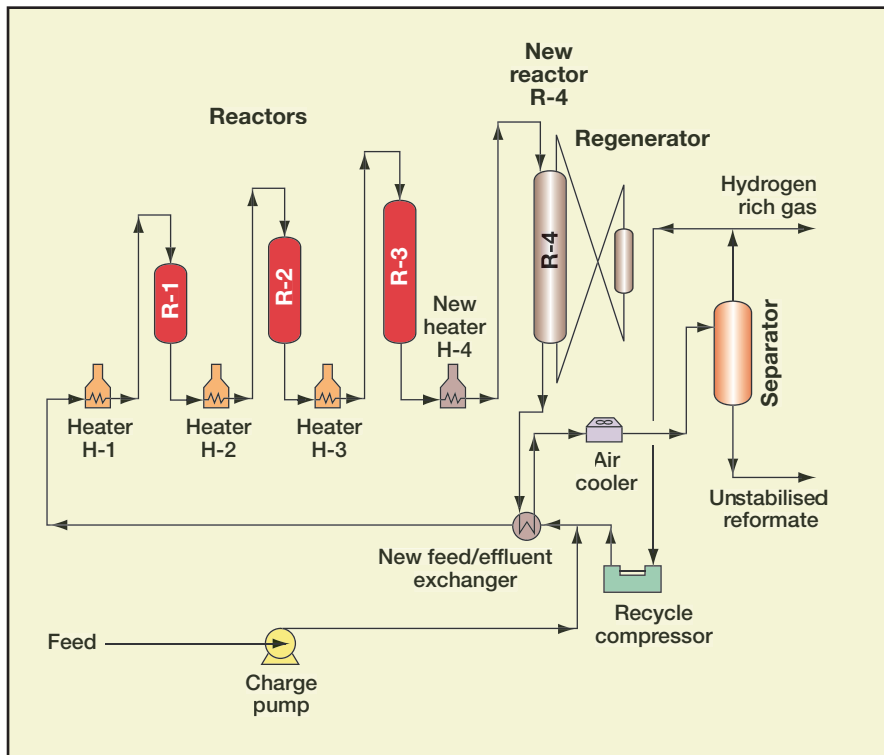


Figure 9 Dualforming flow diagram

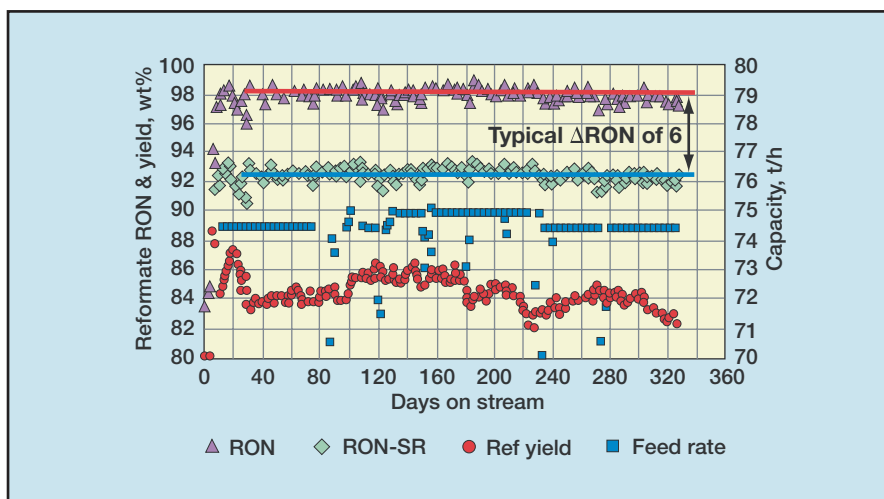


Figure 10 Dualformer commercial data

SR reformer revamp to Dualforming or full CCR			
Scheme:	Existing SR unit	Dualforming	Octanizing CCR
20 000bpd, 100 RON			
Cycle length, month	6	12/cont.	Continuous
Yields, wt%			
H ₂	1.7	2.4	3.1
C ₅ +	76.3	81.9	87.4
Revamp investment, million \$	Base unit	+18	+40
Cat & utilities, million \$/yr	3.1	5.3	7.8
Prod. revenue, million \$/yr	-	14.1	28.4

Table 3

Hybrid design

When considering an existing SR unit that is not equipped to be transformed to CCR, it is still possible to capture some of the benefits of a CCR design. In the mid-1980s, the Dualforming process

was developed and commercialised. This enables the revamping of a conventional reformer with the addition of a new moving-bed reactor and regeneration system to produce higher-octane reformate, plus increased hydrogen

production and yield selectivity at a minimum capital cost. Five Dualformers are currently in operation and others are being designed (Figure 9).

With Dualforming, the objective is to make maximum use of existing equipment, while improving reformate yield, hydrogen production and/or cycle length compared to a SR unit. For an existing three-reactor SR unit, the potential benefits of adding a fourth reactor to increase throughput and/or cycle length are first evaluated. Then, a Dualforming case is appraised to allow for more severe operation. In many cases, significant improvement in catalytic reforming flexibility may be realised at less than 50% of the capital investment costs of a new CCR.

It is well known that reducing operating pressure in a catalytic reforming unit substantially improves the yield of reformate and hydrogen (especially hydrogen). It is also known that lower-pressure operations in fixed-bed units increase the formation of coke on reforming catalyst and significantly reduce cycle life. The Dualforming process addresses both the positive and negative factors of lower operating pressure.

A significant advantage of the process is the maximum use of existing reactor section equipment in the SR catalytic reformer. The revamp includes the addition of a new reactor that operates with continuous catalyst circulation. As shown in Figure 9, the new reactor and regenerator are integrated into the existing reactor train of the conventional reformer and operate at a pressure lower than the original unit and consistent with Pt-Sn CCR catalysts — less than about 17 barg (250psig).

The reduction in unit pressure allows for the use of the more selective Pt-Sn catalyst system in the last reactor, but requires careful evaluation of the recycle compressor so that the unit severity profile, pressure and hydrogen recycle are compatible with the cycle length and yield objectives. In many cases, this will lead to the installation of a low ΔP , high-efficiency feed/effluent heat exchanger to minimise the pressure drop. Other major pieces of equipment involved in the revamp include an additional inter-heater for the new reactor, a booster compressor to export hydrogen at the original design pressure and, of course, the regeneration system.

The configuration shown in Figure 9 allows for the operating pressure to be reduced in the SR section of the unit. The amount of pressure reduction is limited primarily by the pressure drop through the unit and by the existing recycle compressor. The SR section is then operated at a lower severity and

reaction temperature to satisfy cycle length requirements, with the new CCR reactor operating at a higher severity to complete the reaction. In one example, the average reactor pressure of the reformer was reduced from 26 barg (375–220psig).

The overall result of the Dualforming process sees an improvement in both reformat and hydrogen yields and octane performance at a lower capital cost than the CCR process. A comparison of the operating conditions and yields from an SR unit, a revamp to Dualforming and a major revamp to CCR are presented in Table 3.

Data from the five commercial Dualforming units operating since 1987 have demonstrated reliable operation over the cycle length of the fixed-bed portion of the unit. Data from one unit is shown in Figure 10. The reformat octane leaving the fixed-bed reactor (SR) and the final product octane are steady throughout the one-year cycle, with a constant octane boost of 6 RON points across the reactor. Optimising the fixed-bed cycle length with the severity in the CCR Dualformer reactor is a key parameter based upon commercial experience.

The added reactor and regeneration system allow the new, final reactor to operate continuously and at a higher severity than the fixed-bed portion of the unit. But ultimately, a Dualforming unit will be limited by the fixed-bed SR section of the unit, as these reactors still require shutdown for regeneration.

In a variation on the Dualforming design, the new reactor-regenerator system is located downstream from the fixed-bed reactors, separator and recycle

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hydrogen loop. As a result, the new reactor can be operated at a very low pressure, thereby bypassing the constraint of the existing recycle compressor. This configuration is called Dualforming Plus, which also is capable of processing the combined effluent from several fixed-bed units for maximum unit flexibility.

Advances

Advances in CCR reforming (Octanizing/Aromizing) using the latest catalysts (CR 401, CR 702, AR 501) and incorporating the new RegenC-2 regenerator significantly reduce CCR reforming operating costs by lowering catalyst deactivation and attrition, as well as chloride consumption. The process provides high on-stream unit availability with maximum liquid yields and high co-production of hydrogen to satisfy the reliability and hydrogen requirements of new ultra-low-sulphur fuels hydrotreating units. These advances are demonstrated by 14 new CCR unit references since 2004 and ten references in 2005 alone.

Some refiners have opted to invest in transformable units that operate as SR units at a lower capital cost, but with the ability to be converted to CCR operation later to stage their capital investment. This option is particularly attractive if large unit expansion is planned in the future or much higher severity for aromatics production is envisaged.

Not all refiners have the option of investment in new units and require ways to maximise the use of existing assets or staging investments. Existing SR reforming units can benefit from the new RG 682 catalyst and hardware modifications such as Texicap to better use the reactor volume and increase cycle length as well as reformat and hydrogen yields. For large increases in severity and/or capacity, a proven hybrid Dualforming design using an additional reactor with a CCR loop can combine some of the attributes of a CCR system while maximising the reuse of existing SR equipment.

This article is based on a presentation from the 2005 Axens European Refining Seminar in Vienna. Octanizing, Aromizing, Texicap, Dualforming and DualformingPlus are marks of Axens.

Bruno Domergue is product line manager, catalytic reforming and paraffins isomerisation with Axens in Paris, France.

Email: bruno.domergue@axens.net
Jay Ross is technical manager with Axens North America in Princeton, New Jersey, USA. Email: jross@axensna.com

Pierre-Yves le Goff is technical manager with Axens in Paris, France.
Email: pierre-yves.le-goff@axens.net
