Increasing Semi-Regenerative Reformer Performance through Catalytic Solutions

Pierre-Yves Le Goff, Jean de Bonneville, Bruno Domergue and Martin Pike
Axens

Catalytic reforming with fluid catalytic cracking is the backbone for gasoline production. Reforming is also the most important source of aromatics for the petrochemical industry. For gasoline production, despite limitations in aromatics, reforming remains the key process in the refinery. Indeed it is also the main source of hydrogen and, due to the most stringent specification for sulphur in motor fuels, additional hydrogen is needed for hydrotreatment processing.

In order to compete with these new challenges, Axens has launched new catalysts for semi-regen and CCR units. For semi-regen units three new promoted bimetallic catalysts have been commercialised. The platinum loading of our workhorse RG 582 has been reduced without any adverse impact on selectivity or stability. In addition, the use of new production technology has enabled Axens to commercialise a new Pt/Re promoted bimetallic catalyst, RG 682. The RG 682, like RG 582 is available at two different platinum loadings.

The RG 682 series benefits from new manufacturing techniques, which ensure optimised interactions between the various components at the nanometer scale. Nano-scale product control results in improved synergies of the active species resulting in higher activity, selectivity and stability while retaining chloride retention properties.
**Introduction**

This paper describes our new fixed bed reforming catalyst RG 682, RG 682 A, and RG 582 as well as the benefits obtained with Texicap™, our proprietary reactor internals, together with Axens technical services.

**Progress in reforming catalysts**

**Introduction**

From 1953 to 1967, platinum impregnated on a slightly chlorinated gamma alumina support made up the conventional bi-functional monometallic reforming catalyst. In 1969, the first industrial results were obtained with a rhenium promoted platinum catalyst. The significant improvement obtained by using other metals, such as rhenium, in combination with the primary reforming catalyst metal, platinum, prompted a rapid development of bi-metallic or multi-metallic catalysts.

Axens’ first bi-metallic platinum-rhenium catalyst, RG 482, was followed in 1994 by RG 582. This new product was the first industrial PtRe multi-metallic catalyst, providing maximum \( C_5^+ \) and hydrogen yields combined with excellent stability in both semi-regenerative and cyclic reformers. RG 582 has shown outstanding results in a wide variety of commercial applications worldwide.

Axens is currently introducing a new platinum rhenium multi-metallic catalyst into the market. **RG 682** is designed for semi-regenerative reformer applications, but can also be applied to cyclic reforming service. RG 682 represents an important development within our reforming catalyst portfolio.

**Chemistry of RG 682's Outstanding Performances**

The addition of rhenium to a platinum/alumina catalyst dramatically improves the stability (cycle length) of the catalyst by decreasing both the rate of coke formation and its toxic effect on catalyst activity. RG 682 exhibits excellent yields and activity even at higher coke levels. Other promoter metals, such as tin or germanium, enhance hydrogen and \( C_5^+ \) yields by suppressing hydrogenolysis of paraffins and alkyl aromatics to light gases, but these catalysts show poor stability, i.e. similar to platinum monometallic catalysts. This is due to reduced hydrogenolysis of coke precursors resulting in the deposition of coke in a mono-layer over the metallic species.

Commercial attempts to use promoter metals such as tin and germanium for fixed bed applications have either failed to meet the yield and stability objectives, or they have not had sufficient activity or they have been exceedingly difficult to regenerate. Now with **RG 682**, a moderated tri-metallic catalyst, it has been demonstrated that these performance barriers have been overcome. **RG 682** is a moderately skewed Pt/Re catalyst that combines a third promoter metal and is now recognised as a definite breakthrough by the industry. The result is:

- Improved yield
- Increased stability
- Increased activity
- Ease of regenerability
The third metal moves the yield profile directionally toward that achieved with tin or germanium but without any of the disadvantages noted above. To the contrary, yield and stability are excellent, and regeneration is easy.

A significant factor in improved liquid yields is the metal function provided by the active phase. The metal function that has been moderated is that leading to hydrogenolysis which converts $C_6^+$ materials to undesirable $C_5^-$ compounds. Such hydrogenolysis moderation also suppresses benzene formation by hydrodealkylation of heavier aromatics in the tail reactors.

RG 682 uses new technology to improve the interaction of the catalytic metal species on the alumina carrier, impacting the catalytic properties at the nanometer scale to produce the results outlined above. Axens’ nanotechnology has enabled optimisation of the metal phase interaction and the surface characteristics of the alumina carrier.

Figure 1 shows typical full cycle $C_5^+$ yield profiles for various catalyst formulations. A balanced Pt/Re catalyst such as RG 482 has a start of cycle (SOC) yield equivalent to a monometallic platinum catalyst. But as the cycle progresses, it shows greatly improved average yield and a longer cycle length. The impact of the rhenium metal is described above. The addition of tin (Sn) or germanium (Ge) improves SOC yield, but has zero impact on yield stability, thus these catalysts exhibit cycle lengths similar to the mono-metallic catalyst. However, the addition of the third metal in RG 582 adds approximately 1 wt % higher yield at SOC and a comparable cycle length as a standard Pt/Re bimetallic catalyst.

**RG682** provides 0.6 to 1.0 wt % increase in $C_5^+$ yield over RG 582. As it is a moderately skewed catalyst, it brings, in addition, a greater resistance and tolerance to coke thereby extending the cycle life by more than 35 % over a ‘classical’ balanced bimetallic Pt/Re catalyst.

**Figure 1 : Typical Full Cycle $C_5^+$ Yields**
**Improved Hydrogen Production**

As a result of its lower hydrogenolysis activity, **RG682** produces 5% more hydrogen at 98 octane compared to RG 582. This is a considerable performance considering that RG 582 was already recognised as the leading hydrogen improvement catalyst in commercial applications. **RG682** also exhibits the same sulphur tolerance as RG 582 and can withstand, over short periods, sulphur levels of 1 wt ppm in the feed, although typical feedstocks should be in the range of 0.2 – 0.5 ppm.

**IFP’s Performance Comparison**

The following summarises the test data obtained at IFP’s development facilities in France. Figure 2 shows stability and activity testing for **RG682** in comparison with RG 582. In commercial operations, RG 582 has proven to be at least as stable as a standard balanced Pt/Re catalyst, and more stable than competitive unbalanced catalysts in the presence of even minor quantities of sulphur.

![Figure 2: Activity and stability benefit with RG 682 compared to RG 582](image)

Pilot scale testing shows RG 682 can reliably extend cycle life by 35 – 40% over RG 582. The activity gain at constant octane is 3 – 5°C and is maintained throughout the performance test. An additional extended cycle length is likely due to the lower start of run temperature. If no mechanical restrictions exist, this increased activity can be used instead to increase the capacity or the operating severity of the unit.

**RG682** was also tested for C₅⁺ yield compared to RG 582. The latter catalyst is commercially known to show a yield gain of 1 wt % C₅⁺ versus standard balanced Pt/Re catalysts. The results of this constant octane test are shown in Figure 3. After an initial stabilisation period, RG682 shows a significant gain in C₅⁺ yield, which is maintained throughout the test period. In fact, the cycle average difference between these catalysts is greater than the 0.6 wt %.
Figure 3: Selectivity benefit obtained with RG 682 compared to RG 582

Table 1 summarises the results obtained with RG 682 compared to previous generation catalysts.

<table>
<thead>
<tr>
<th>Yields (wt%)</th>
<th>Standard PtRe</th>
<th>RG 582 Series</th>
<th>RG 682 Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Base</td>
<td>Base + 0.12</td>
<td>Base + 0.18</td>
</tr>
<tr>
<td>C₁+C₂</td>
<td>Base</td>
<td>Base – 0.5</td>
<td>Base – 0.5</td>
</tr>
<tr>
<td>C₃+C₄</td>
<td>Base</td>
<td>Base – 0.7</td>
<td>Base – 1.2</td>
</tr>
<tr>
<td>C₅+</td>
<td>Base</td>
<td>Base + 1.0</td>
<td>Base + 1.6</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Base</td>
<td>Base + 0.4</td>
<td>Base + 1.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>Base</td>
<td>Base – 0.2</td>
<td>Base – 0.2</td>
</tr>
<tr>
<td>Temp. SOR*</td>
<td>Base</td>
<td>Base</td>
<td>Base – 3°C</td>
</tr>
<tr>
<td>Stability</td>
<td>1.0</td>
<td>1.0</td>
<td>1.35</td>
</tr>
</tbody>
</table>

*Activity improvement is directly proportional to the reduction in the start of run temperature (SOR).
Pressure = 10 barg, RONC = 98, WHSV = 3/h, H₂/HC = 3, PNA = 52/33/15

The data shows that RG 682 is truly a step out in terms of performance. The increased yields, improved stability and increased activity make this the catalyst of choice for all semi-regenerative reformer applications.
Low platinum catalysts

Axens has significantly improved the production process, enabling the commercialisation of a 10 wt % lower platinum-loaded catalysts without reduction of either the activity or the stability. The new RG 682 A and RG 582 A catalysts exhibit excellent performances with respect to the higher loaded versions. The platinum and rhenium loading for each catalyst are shown in Table 2. For all four catalysts, the loading densities are 0.6 and 0.69 respectively for sock and dense.

Table 2: Pt and Re loading for our promoted bimetallic catalyst portfolio

<table>
<thead>
<tr>
<th></th>
<th>RG 582 A</th>
<th>RG 582</th>
<th>RG 682 A</th>
<th>RG 682</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt loading (wt %)</td>
<td>0.27</td>
<td>0.3</td>
<td>0.27</td>
<td>0.3</td>
</tr>
<tr>
<td>Re loading (wt %)</td>
<td>0.27</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The choice between the higher and lower loaded platinum and rhenium catalysts depends on two factors: average feed sulphur content and regularity of sulphur upsets. The 500 series, due to its lower rhenium content, is more sulphur tolerant. Thus, the 600 series is preferred when the feed sulphur content is likely to be low. Likewise, when there is a low frequency of sulphur upsets in the unit, the lower platinum loaded “A” series is the preferred option due to the lower platinum inventory. This catalyst selection philosophy is summarised below.

![Catalyst Selection Diagram](image)

**Figure 4: Selection of Axens promoted bimetallic fixed-bed reforming catalysts.**

**Advances in Commercial Reforming Catalysts**

The **RG 682** and **RG 682** catalysts can provide significant improvements in both C\textsubscript{5}+ and H\textsubscript{2} yields as well as increase cycle length in semi-regenerative units. With a significant number
of satisfied customers already using Axens’ tri-metallic catalysts, we have the commercial experience attesting to the performance benefits that can be achieved.

**Texicap, an innovation approach to increase unit performance**

**Introduction**

Fixed-bed radial flow reactors are used wherever low-pressure drop is critical to good performance, such as in fixed-bed reforming units. It has been standard practice in radial reactor design to bypass approximately the top 15 per cent of the catalyst bed. This is done intentionally to prevent reactants from short-circuiting the catalyst after the bed settles. Catalyst settling during the course of the run generates a gap between the top of the bed and cover plate. Were it not for the shroud extending down into the bed, the reactants would pass preferentially through the gap. In addition, because of the very high residence time due to poor flow dynamics in the shroud volume, the catalyst loaded at the shroud level attains very high coke levels, much higher than the average (figure 5).

![Image of Axens catalysts](image)

**Figure 5:** Computational Fluid Dynamic (CFD) calculations showing the coke distribution without and with Texicap™. The high coke level, red colour, appears in the shroud region (without Texicap).

The coke, found in the shroud region, is very difficult to burn during regeneration. In addition, centre pipe grid damage is frequently observed in the top of the bed. This is due to the final coke burn at high oxygen content. Therefore, expensive reforming catalyst (unused platinum inventory) and reactor volume are wasted. Responding to this problem, IFP in the early nineties developed a cost-effective way to recover unused bed volume.
**Texicap™ how does it work?**

The conventional metal shroud assembly is replaced by Texicap™, a flexible flow-guide that moulds to the shape of the top of the bed. The flow-guide settles along with the bed so there is no further need to design dead space; the formerly dormant catalyst section is now completely operational. Compared with original flow conditions, reactor pressure drop is lower, now that the reactants flow through a greater catalyst bed cross-section. Or, viewed differently, the reactor can accept 15 per cent more feed.

The gas flow through the catalyst bed is even and flow dynamics are nearly perfect from top to bottom through the homogeneously loaded bed, ensuring a long run without channelling.

**Texicap™ what is it?**

Texicap is an engineered composite of refractory fibres and fillers containing no asbestos, Figure 6 and 7. It is impermeable and withstands the severe operating conditions of multiple regenerations encountered in reformers as well as the hydrogen/hydrocarbon atmosphere. Installation and removal are easy, requiring **about one-tenth the manpower and time required to remove and replace the shroud and cover assembly.**

The first Texicap was installed in 1992 at the IES refinery in Italy. Since then, this application has been extensively implemented. In Europe alone, nearly 40 radial reactors in major refineries (Agip, Elf, Repsol, Shell, TotalFinaElf, etc.) were upgraded with this technology.
Cost reduction with Texicap

Texicap™ improve the unit performance and economics due to a better fluid dynamics and shorter down time 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
- Centre-pipe maintenance is reduced
- Downtime for catalyst change out is reduced, due to rapidity of installation and removal; **turnaround time reduced by at least 50 hours** for a four reactor reformer, with a corresponding gain in throughput.

For a standard reforming unit, approximately 15 % of the catalyst is not utilised. If a 40 m³ (1,410 ft³) unit is considered, 6m³ (212 ft³) of catalyst could be removed while retaining the same throughput. The platinum saving in weight and in euros are indicated in the following Table 3. Added to this savings is a gain in > 50 hours production time, roughly 3,000 tons of additional product. Overall, a gain in excess of one million euros is accounted. Texicap is a powerful technology tool to improve radial fixed bed unit performance and profitability.


**Table 3: Platinum saving with Texicap™**

<table>
<thead>
<tr>
<th>Inventory reduction, Kg</th>
<th>RG 582 A</th>
<th>RG 582</th>
<th>RG 682 A</th>
<th>RG 682</th>
</tr>
</thead>
<tbody>
<tr>
<td>Financial Reduction*, Euros</td>
<td>220,810</td>
<td>245,345</td>
<td>220,810</td>
<td>245,345</td>
</tr>
</tbody>
</table>

* Platinum cost: mean value for 2001 – 19,754 €/kg

**Axens’ Tech Service**

**Catalyst analysis**

Catalyst sampling during operation is helpful to improve operation and to anticipate catalyst replacement. For example, if the chloride level on the catalyst is not properly adjusted, the activity of the reforming catalyst for methylcyclopentane conversion is greatly reduced. As a consequence a periodical analysis of the catalyst is necessary to ensure optimal unit performance.

![Axens catalyst analysis](image)

**Figure 8: Effect of the chloride content on the catalyst on the conversion**

Axens commercialises a highly robust and reliable technology for sampling service and performs a large palate of chemical and physical analysis, Figure 8. Based on our extensive experience on unit follow up, we have provided extensive tech service for unit optimisation.
Continuing research and development, improved production methods and technology, discreet technological innovations and return from field operations have enabled the optimisation of the operation and the financial return from semi-regenerative reformers. Built on the success of the semi-regenerative catalyst workhorse, RG 582, which is present in over 50 commercial units, Axens has commercialised three new catalysts: RG 582 A, RG 682 and RG 682 A. Three units are currently operating with RG 682/RG 682 A.

Tech Service is a key synergy between the Process Licensing and Procatalyse Catalysts & Adsorbents Business units in Axens. The combination of Axens catalysts, Texicap internals, catalyst sampling devices and process tech service for unit optimisation is a powerful access to performance enhancement and improved financial return on employed capital in the refinery.