Question 44: What are the operating parameters, including water or chloride additions, to adjust and monitor on a continuous catalytic regeneration reforming unit when it is required to operate for a short period of time (hours/days) with the regeneration section shut down (for instance if operating in low-coke mode)?

Ujjal Roy (Indian Oil Corporation)

We have four CCR/Platformers in our refineries. While two operates for gasoline production, one operates in mix mode i.e., for BT as well as for gasoline production. The other solely operates for para-xylene production.

We have experienced regenerator outage on many occasions from few hours to as high as 6-7 days. Moisture content in recycle gas is normally between 15 to 35 ppm in all these units when regenerators are under operation. During regenerator outage, even for longer duration, we never had to resort to water injection. At the most, we observe moisture reduction in recycle gas is by about 5 ppm from normal operation. As soon as regenerator is out of line, we immediately start chloride dosing in feed and closely monitor recycle gas moisture and chloride content. HCl in recycle gas is maintained at normal operating level.

In addition to proper water/chloride balance, we take various other actions to ensure limiting coke on catalyst within design level of regenerator capacity (which is generally designed for 6% wt. max. coke on spent catalyst). These actions are as below:

a) In one of our gasoline mode platformers, feed contains about 40% of FCC gasoline. We minimize FCC cracked gasoline in feed by optimizing FCC operation. Cracked naphtha coking rate is almost 1.5 times as compared to that of straight-run naphtha.

b) We reduce platformer throughput and RIT but also try to change the crude mix to get higher N+2A in order to get desired conversion and target RON. This may require costlier low sulphur crude processing as in our case is Bombay High. Gasoline production is partly made up by higher back blending of desulphurized straight-run naphtha having higher base RON.

c) With reduction in Platformer throughput, we also resort to increasing separator pressure and recycle ratio in order to get higher partial pressure of hydrogen by about 10-20% within available cushion of the equipment's. This helps in containing coke build-up during longer regenerator shutdown and sustain stable operation.

With all these measures, we have observed that the coke build-up rate on catalyst is about 0.25 – 0.3 wt.% of catalyst per day. At this rate of coke build-up, it helped us to continue operation without regenerator for as long as 7-8 days. When we started the regenerator back, we found that coke on the spent catalyst was about 6% wt. as against 4% wt. when the regenerator was shutdown. In one such occasion, in one of the platformers, the coke on spent the catalyst went up to as high as 10% presumably due to inappropriate control. Normally chloride on spent catalyst at the point of starting back the regenerator was found mostly between 0.9 – 1%.

When regenerator is out for a longer period, it is utmost important to control the coke laydown within the capability of regenerator design. High coke on catalyst may lead to slippage of coke to oxychlorination zone when the regenerator is started. It can also lead to high burning delta temperature. This in turn can change phase of the catalyst from gamma to inactive alpha alumina and permanently damages the catalyst. This happened in one of our refineries in a particular instance, when coke laydown was significantly high as compared to maximum recommended value resulting in presence of alpha alumina in regenerated catalyst after start of regenerator. In such circumstances, when regenerator is started back, coke burning rate to be kept well within design to avoid permanent catalyst damage.

In case, water is injected (that we have never done in any reformer) along with chloride in feed during regenerator outage, continuous monitoring of moisture and HCl in recycle gas should be done to ensure proper dosing control. High chloride will lead to excessive cracking. Also, if the catalyst is old and have considerable reduced surface area, chloride retention on the catalyst will be lower. Any excess chloride thus would land up in recycle gas. This can lead to corrosion related problems in downstream equipment and units.

Also, with increased chlorine retention on catalyst, activity of the catalyst increases while selectivity decreases. Hence, one has to optimize dosing based on the yields of desired products and conversion which is already affected by higher coke make when regenerator is down.

Some catalyst vendors offer high stability catalysts which tend to form lower coke at given conditions. If one is operating platformer without regenerator frequently, he can look for such catalyst in next replacement. But also new catalysts with higher surface area will make higher coke initially.

I would also suggest that during regenerator shutdown, delta T across reactors should be in focus along with parameters like H2 yield and purity, C3 – C4 yields. Feed blend, throughputs and severity should be properly managed based on these parameters. In all our refineries, naphtha and gasoline production are optimized through varying operation of hydrotreaters, reformers, isomerization, bensat and treatment units. These give us flexibility for feed management of both intermediate and finished products blending streams.

Olivier Le-Coz (Axens)

For a very short period of time (less than one day), there is no need to inject chlorinating agent with the feed to maintain the chlorine level on the catalyst.

For longer periods, chlorinating agent shall be injected (at about 0.4 wtppm in the feed) to maintain as close as possible to 1 wt% of chloride on the catalyst. HCl content in the recycle gas shall be carefully monitored and be maintained below 3 vol ppm. Water injection with the feed must be adjusted to maintain 20 vol ppm of moisture in the recycle gas. This moisture level is needed to ensure good chlorine spreading over all the reactors (and not only in the first one) by establishing proper H2O / HCl equilibrium and preventing local HCl excess. This will also allow minimizing cracking activity. Depending on the coke make, WAIT / catalyst circulation rate / H2/HC ratio should be adjusted to maintain the coke yield on the catalyst within the suitable range for the regenerator to be able to operate properly once this section is restarted.

Michael Windham (UOP)

When the CCR is shut down for more than a few hours, UOP recommends injecting chloride agent into the feed. Injection rates are generally in the 1.0 ppmw based on feed rate. Water injection is not normally required. For extended down time, operators should monitor reactor delta temperatures and adjust reactor temperatures or feed rate if the dT, s and reformate octane are declining.

Erik Myers (Valero)

In general, a significant maintenance downtime (7 days) would require the addition of chloride into the Reforming unit feed. Valero does not usually add water to the CCR unit feed. What may not be realized is the chloride uptake of the catalyst declines as the surface area decreases. In general, the chloride injection target, calculated as wt ppm chloride injected in the feed, needs to be increased over the life of the catalyst.

In a coke limited unit, feed should be cut to increase hydrogen to hydrocarbon and suppress coke lay down such that upon restart of the regenerator the coke is less than 7 wt%. Valero uses a 60% coke lay down distribution into the last reactor’s catalyst during periods of no catalyst circulation. The challenge is when to increase severity after restarting catalyst circulation and regeneration. Valero uses the following guidelines for reintroduction of full severity on the unit, once the last reactor catalyst is regenerated, 50% of the rate/octane cut is added back, when the catalyst from the second to last reactor is regenerated 30% of the rate/octane is added back and the last 20% of the severity is added back when the coke on catalyst goes below 6.5 wt%. In this manner the production of the CCR is maximized during the restart. Companies that do not model the reactor coke profile correctly will go from high coke to low coke in the course of the restart which has economic penalty.

Soni O. Oyekan, PhD (Marathon Petroleum Company)

The question is broad as the time involved in the low coke operation mode and the spent catalyst and regenerated catalyst chlorides before the outage of the regenerator are important factors. We can assess the delta chloride (regenerated catalyst chloride minus spent catalyst chloride) and use a trend of that data to assess the dryness of the reactor system. The dryness of reaction system can also be determined from the recycle gas water and HCl data for the catalytic reformer. Another factor is the relative state of the metal and acidic functionalities of the catalyst as a consequence of unsteady state cycling between black and white burn regenerator operations which could have negatively impacted platinum dispersion and the metal functionality.

While addition of water and chloride to the feed can give moderate boost in catalyst activity, there could be penalties associated with deceased productivity and poor selectivity as a consequence of excessive hydrocracking for the continuous catalyst regeneration reformer. However, the refiner could be limited with respect to proper water/chloride management, if the refiner has not established a good database on the performance of the catalyst in their reformer as a reference and simply adding water and chloride may actually be detrimental.

To make relevant, process enhancing water/chloride management moves requires that a good reference database of the reformer performance is available so as to permit comparing performance relative to reference as some of the water/chloride management steps are being made.

For short periods of regenerator outage, the refiner can assess or determine spent catalyst chloride levels and could add chloride if the expected levels are lower than catalyst chloride operating targets from experience. I would, however, not recommend adding water or chloride during short periods of outages for the regenerators of less than one day.

For longer periods, water/chloride management can be affected based on some knowledge of the items that I discussed earlier.

The items again are:

• Good reference data on catalyst performance during steady state white burn regenerator operations

• Good or reasonable information on metal and acid functionalities states of the catalyst via platinum dispersion and delta catalyst chloride data

• Reliable data on recycle gas water and hydrogen chloride.

A key consideration for water/chloride management steps when the regenerator is not operating is ensuring that the catalyst is not overloaded with chloride thereby exacerbating metal and acid functionalities imbalance which may have occurred due to the unsteady cycling of black and white burn regenerator operations.

Lastly, some considerations should be given to the effect of added water and chloride on potential increased fouling and corrosion in the product separation section (condensers, compressors, stabilizers) of the catalytic reformer. Additionally, the net hydrogen gas HCl could also increase, and suitable chloride guard systems should be in place to help manage the potentially higher HCl in the net hydrogen gas.

Blending

Catalysts

Catalytic Reforming

Chlorides

Compressors

Corrosion

Crudes

Fouling

Hydrogen

Octane

Operations

Optimization

Process

Reactor Vessel

Reforming

Regenerator

Reliability

Year

2011