Question 36: What changes have you made to the C5/C6 Isomerization unit to comply with the new benzene regulations; what changes have you made to the refinery operation; and what have been your challenges and successes of implementing the new configuration?

Olivier Le-Coz (Axens)

More severe regulation in term of Benzene in the gasoline pool can lead to increase the Benzene content to the C5/C6 isomerization unit. This can happen in two different ways.

The refinery process operation can be modified to decrease the benzene precursors content in the heavy naphtha to the Reformer. This is achieved by increasing the light naphtha end point in the topping lights ends naphtha splitter, light naphtha being the Isom unit feed. At the same time C7+ in the Isom feed must be limited to 2 – 3 vol% as those products will undergo undesired hydrocracking reactions in the Isom reactors. With such a scheme, straight run naphtha Benzene (native Benzene) is basically treated in the Isom. This approach can typically be applied in the frame of a new project.

When the “pre-fractionation” scheme cannot be implemented or if it cannot allow reaching the overall pool Benzene specification, a “post-fractionation” option can be implemented. It consists in splitting the reformer product and recover a light Benzene rich reformate which will be treated in the Isom unit in blend with the light straight run naphtha. Depending on the Isom unit existing configuration, some modification to the hardware may be required or not. As a matter of fact, Benzene concentration at the Isom reactors inlet should better not exceed certain value to ensure proper operation and performances of the Isom catalyst (about 4 vol%).

-If the Isom unit is equipped with a recirculation, the recirculated stream acting as diluent may allow maintaining Benzene below the desirable value at the reactor inlet. The extra Benzene amount in the feed will be hydrotreated by the Isom catalyst without disturbing too much the operating conditions and without preventing suitable isomerization rate to be achieved.

-If the Benzene content at the inlet of the reactors cannot be maintained low enough (too low or no recirculation), a dedicated Benzene saturation reactor must be added.

In the case of new units implementation, those schemes have proved to work very well. In the case of revamp projects, existing equipment modifications or idle equipment reuse, a through basic design study upfront including the catalytic aspects is strongly recommended.

Brad Palmer (ConocoPhillips)

In general, refineries with C5/C6 Isomerization units or Aromatic Extraction units have increased feed

rate and/or benzene content to these units. Reformer octane has gone down due to ethanol blending but, in most cases, Isom octane demand has remained strong. The primary successes include implementing these projects safely and achieving our benzene reduction requirements. Additionally, heavy reformate blend qualities have improved which has made blending premium gasoline easier and has provided additional opportunities for blend component sales.

A number of technology options were chosen by ConocoPhillips refineries to meet benzene regulations according to the existing configuration and site economics. These options include revamping Aromatic Extraction Units (AEUs) to increase feed and benzene production capacity, sending light reformate or heart cut to other AEUs, modifying C5/C6 Isom units to include benzene saturation reactors, new benzene saturation unit construction, reducing benzene production through prefractionation and use of credits.

All completed projects are working, some with very few operating problems and a few with requiring design modifications and/or operating changes. Operating, design and reliability issues continue to be worked to improve unit performance; a few specific examples are provided below.

Isomerization Unit Challenges

-When all benzene saturation reactors are complete, two will have Pt catalyst and four will have nickel catalyst. One of the reactors will have changed from Pt to Ni.

-The units that added a benzene saturation reactor in front of their Isom reactors have had challenges controlling temperatures profiles of all three reactors especially when liquid recycle is added or removed.

-Isom units have heavier feeds (increased X-Factor). One unit has and XF of 30 lv% average (35 lv% highest) and 9 lv% Benzene Average (10 lv% highest). Another unit has an XF of 25 lv% average (27 lv% highest) and 5 lv% Benzene Average (10 lv% highest).

-Determining when and how much liquid recycle is necessary for safe operation while maximizing fresh feed throughput has taken time. Vendors advertise an upper benzene level of 5 lv% to the inlet of a benzene saturation reactor. While we have gone a little higher by lowering the inlet temperature to accommodate the exotherm, this is a good rule of thumb.

-Increased unit rate can impact dryer operation by fluffing up-flow desiccant beds. Higher rates increase HCl loading to existing caustic scrubbers; less than adequate neutralization can lead to corrosion problems.

-Benzene saturation catalyst has been deactivated or poisoned by feed (organic sulfur, H2S, FeS, Chlorides) or hydrogen purity (CO and CO2) problems.

Aromatic Extraction Unit Challenges

- Changes in feed quality have required operations to find new equilibrium; one unit has reported bigger swings in aromatic content with new feed streams.

- Stripper foaming has occurred in one unit.

Ujjal Roy (Indian Oil Corporation)

In India, the benzene specification in gasoline is 1 vol.% max. In order to meet this specification, number of changes in the refinery configurations have been done. (a) Light Naphtha splitter has been introduced to produce C-5 & C-6 isomerization feed. (b) Naphtha splitter modified to reduce Benzene precursor from Reformer feed Naphtha. (c) Reformate splitter has been installed to separate Benzene from the Reformate. Over and above FCC gasoline being a component of Gasoline, for reduction of Benzene, a FCC gasoline splitter has been put to take away the Benzene rich cut called Heart Cut from Gasoline. For meeting benzene regulation in the Gasoline, Isomerisation unit has been designed with catalysts having dual functions – Isomerisation and complete saturation of Benzene. The metal sites are used for saturation of benzene and acid sites are used for isomerisation of C-5/C-6. Up to 9.8 vol.% benzene in feed, catalyst is able to saturate to nil level of benzene in isomerate.

Erik Myers (Valero)

The Valero approach has been to consolidate the benzene rich streams from various refineries and capture benzene as a product stream. This has been accomplished through use of a side draw stream from the reformate splitters and then feeding these streams through a centralized benzene extraction unit.

Print as PDF:

Tags

Aromatics

Blending

Catalysts

Chlorides

Corrosion

Feed Quality

Hydrogen

Isomerization

Octane

Operations

Poisoning

Process

Reactor Vessel

Reforming

Reliability

Year

2011