Consider advanced technology to remove benzene from gasoline blending pool

Under present clean-fuel regulations, specifically Mobil Source Air Toxics II (MSAT II), US refiners must reduce the benzene content in gasoline to 0.62 vol% on an average annual basis. This rule went into effect Jan. 1, 2011, for large refiners; small refiners received deferments until 2015. In Europe and many other countries, a 1 vol% maximum benzene level in gasoline is also in effect. Other regions are expected to adopt similar clean-fuel regulations. For refiners, the challenge is to meet these tightening gasoline specifications for benzene cost-effectively without significant octane loss.

**CHALLENGES**

Several approaches are available to reduce benzene levels in finished gasoline. Naphtha reforming is the predominant refinery benzene source. Accordingly, preventing the formation of benzene in the reformer is accomplished by prefractionation of the naphtha feed by removing benzene precursors. However, for many refiners, prefractionation of the reformer feed does not provide sufficient benzene reductions to achieve the 0.62 vol% in the gasoline pool. Alternatively, converting the reformer-produced benzene is done downstream of a reformate splitter. Benzene containing the light-reformate fraction from this splitter is sent to a hydrogenation reactor where benzene is converted to cyclohexane. Both strategies incur octane loss and add extra burdens onto the hydrogen balance for the refinery.

A third approach is benzene extraction for the petrochemical market. While petrochemical benzene can be an attractive product, significant investment is required to recover benzene unless the refinery has existing facilities or spare capacity for such a process. It is very difficult to justify this investment on a small scale.

An alternative technology, reformate-alkylation process, can provide a low-cost solution for refiners to meet the benzene regulation without the octane loss and hydrogen debits associated with other processing options.¹

**CALUMET SUPERIOR REFINERY**

The refinery in Superior, Wisconsin, was acquired by Calumet Superior, LLC, in October 2011. At that time, the benzene-reduction project was in progress. The Superior refinery has a nominal crude capacity of 36,000 bpd, along with a semi-regenerative catalytic reforming unit with a capacity of 8,000 bpd. Prior to the acquisition by Calumet, this refinery was managing the MSAT II benzene compliance with reformer feed precursor removal through a naphtha splitter installed upstream of the reformer in 2010. In addition, this refinery purchased credits from other refineries within the organization’s network. The decision to install technology was made in 2010. Initially, it was economically driven to counter the losses from the reduced reformer feedrate. Later, the new unit facilitated the sale of the refinery, as purchasing benzene credits became a moot issue. In the decision-making process, octane losses were mostly weighed against necessary investments to increase hydrogen production due to losses via the reformer. At this time, with the reformate-alkylation unit in full operation, this refinery easily met the 0.62 vol% specification without requiring credits.

**New technology.** The advanced reformate-alkylation process catalytically converts benzene into high-octane alkyl-aromatic blending components by reacting a benzene-rich stream with light olefins, such as ethylene or propylene.¹ ² In a typical application, the new process reduces benzene concentrations in reformate by reacting benzene contained in a light-cut reformate with refinery-grade propylene from a fluid catalytic cracking (FCC) unit over a proprietary zeolite catalyst. Typical benzene concentration in a light-cut reformate, produced by the reformate splitter, ranges from 10 vol% to 30 vol%. **FIG. 1** is a simple flow diagram of the new reformate-alkylation process. Key features include:

- **Fixed-bed catalyst technology.** This advanced process uses a fixed-bed, liquid-phase reactor with low utility require-
ments. The reactor can be a single bed (stage) or multiple beds, depending on the benzene content of the feed and desired benzene conversion. In revamp projects, it is possible to retrofit existing tubular or fixed-bed reactors for the new application.

- **Catalyst.** The process uses a proprietary high-activity zeolite catalyst with long cycle lengths. In addition, the catalyst is regenerated ex-situ to further extend service life.

- **Stabilization.** Propane fed to the unit with propylene is removed from the reformate-alkylation product in a stabilizer. It can produce a propane product of HD-5 quality. Product from the reformate-alkylation unit is a light reformate with a reduced Reid vapor pressure (Rvp).

Besides benzene reduction, the process provides several advantages. The reaction of benzene with light olefin results in a volume swell, which largely depends on the benzene content of the feed and degree of benzene conversion. Also, an octane gain of 2 to 3 numbers of (R+M)/2 in the total reformate is typical. The advanced technology offers reformer flexibility, since it allows refineries to process the full-range naphtha feed in the reformer, thus increasing hydrogen production along with significant octane gain.

**THE PROJECT**

Before selecting the advanced reformate-alkylation technology for the project, the licensor performed a pilot study using reformate provided by the refinery. With the pilot-plant product, the refinery conducted blending studies to verify the product properties and blending value. The refinery evaluation matched the estimates provided by the licensor. A technology license was executed in July 2010 and preparation began for the new process design. Since the refinery regularly
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The operation of the new unit was straightforward and easy to control. Minimal staffing is required, one board/field operator per shift. The unit is operated without any online analysis, and one daily set of samples. Performance exceeded design expectations, in terms of benzene conversion and propylene consumption. The product quality is consistent with projections made at the onset of the project. Calumet benefited from an increase of about 4 points octane (R+M)/2 across the unit, which is equivalent to an increase of about 2 to 3 points on the basis of total reformate. The new unit has enabled Calumet to improve the hydrogen management within the refinery. The Calumet Superior reformate-alkylation unit is designed to process 5,500 bpd of feedstock.

Benefits to the Superior refinery. The new reformate-alkylation unit was designed, constructed and commissioned on an aggressive project timeline. This project applied creative and forward-thinking execution strategies. The new unit had an installation cost of approximately $19 million, within the original budget allocated at the early stages of the project. With the new unit at the Superior refinery, Calumet complied with the MSAT II regulations for benzene. In addition, the project provided several economic benefits with a simple investment payback in approximately 20 months:

- With the new technology, Calumet meets benzene compliance while allowing for full reformer operation. Recovering more hydrogen at the reformer has averted installing a hydrogen unit.
- With the additional octane increase, Calumet can operate the reformer at less severity to produce more gasoline volume.
- With the new unit, benzene compliance is achievable, as shown in **Fig. 5**. The benzene level is consistently maintained below 1 wt%. When the product is blended in the gasoline pool, the Calumet refinery meets the 0.62 vol% maximum benzene level.
- The product is fully blendable into the gasoline pool. **HP**

**NOTES**

1. BenzOUT reformate-alkylation technology was developed by ExxonMobil Research and Engineering Co. (EMRE) and is licensed by Badger Licensing LLC.
2. IN December 2009, EMRE and Badger agreed to jointly market BenzOUT technology to third parties. Since then, licenses and related engineering services are provided exclusively through Badger.
3. Badger Licensing LLC.

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