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Consider options to lower benzene levels in gasoline

New regulations further limit this aromatic from the refinery blending pool

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Refiners in the US are in the process of planning and executing capital projects to comply with the new Mobile Source Air Toxics (MSAT) II regulations that become effective Jan. 1, 2011. These new rules will restrict the annual average benzene level in the gasoline sold in the US, except California, to 0.62 vol%. California has similar restrictions on gasoline benzene content.

Of the various refinery streams that are blended into gasoline, 70%–85% of the benzene is contributed by reformate from catalytic reforming and 10%–25% by fluid catalytic cracking (FCC) gasoline. Most MSAT II compliance strategies focus on reducing benzene in reformate.

The benzene content in reformate can be changed by either removing compounds in the reformer feed that can form benzene during the reforming reaction or by removing benzene from the reformate via hydrotreating or solvent extraction.

Benzene removal from FCC gasoline is less straightforward. The relationship of feed properties and reaction process conditions that yield various hydrocarbon compounds in an FCC unit is complex. Thus, a straightforward solution for benzene control is less apparent. Further, FCC gasoline contains olefins and heavier aromatics that are the major octane contributors. Any hydroprocessing route focused on benzene reduction would also saturate a significant portion of these compounds.

Several options for lowering the benzene content in gasoline include:

- Reducing benzene precursors in catalytic reformer feed via fractionation
- Saturating benzene contained in light straight-run (LSR) and/or light hydrocrackate
- Installing a reformate splitter to produce a benzene-rich stream followed by hydroprocessing to remove benzene
- Removing benzene from reformate via solvent extraction
- Purchasing benzene credits from other refineries. The maximum average benzene content must still be below 1.3 vol%.

The magnitude of the benzene reduction achievable with the listed options is discussed in a refinery case study. An optimization study to establish the design parameters for a new naphtha fractionator is also investigated. This study considers the sensitivity of the column design to reflux ratio, and light and heavy

naphtha qualities. The tower size is then optimized based on capital and operating costs.

MSAT II regulations. The present benzene content of reformulated gasoline, which represents about one third of all US gasoline, is limited to 1 vol%. The benzene in the balance of the US pool (conventional gasoline) is regulated relative to historical base-line levels. New regulations will reduce the average benzene concentration in gasoline to 0.62 vol%. Since this is a corporate average, standard individual facilities in a refiner's system can have higher benzene levels but are limited to a 1.3 vol% maximum average. Refiners who meet the corporate average standard by purchasing credits must meet the maximum average standard (1.3 vol%) by July 1, 2012. The new regulations also provide controls for portable gasoline containers in 2009 and phased-in controls for cold-temperature exhaust starting in 2010.

■ Reduced benzene levels in blended gasoline will require changes in a refinery's naphtha processing configuration

Benefits of benzene removal. The 1999 National Air Toxics Assessment addressed 177 air toxins and identified benzene as one of the worst.¹ The study concluded that MSATs are responsible for 44% of outdoor toxic emissions and 50% of cancer risks. Benzene was identified as the most significant contributor to cancer risk. People who live or work near major roads or live in houses with attached garages are at the highest risk. By 2030, it is estimated that the MSAT II regulations will be responsible for reductions of air toxics by 330,000 tons and benzene emissions by 61,000 tons. Further, passenger vehicles will emit 45% less benzene and portable containers will emit 80% less benzene. Cancer risks from all MSATs will be reduced by 30% and cancer risks from benzene is estimated to be reduced by 37%.

Benzene in gasoline. Benzene is present in crude oil and condensate, which is a byproduct from natural-gas processing. Benzene is also formed in a number of catalytic and thermal processes within the refinery. Table 1 summarizes the typical concentration range of benzene from various refinery streams.²

Fig. 1 shows a block flow diagram of a notional 150,000-bpsd refinery. Major process conversion units include: isomerization, catalytic reforming, FCC, alkylation and delayed coking.

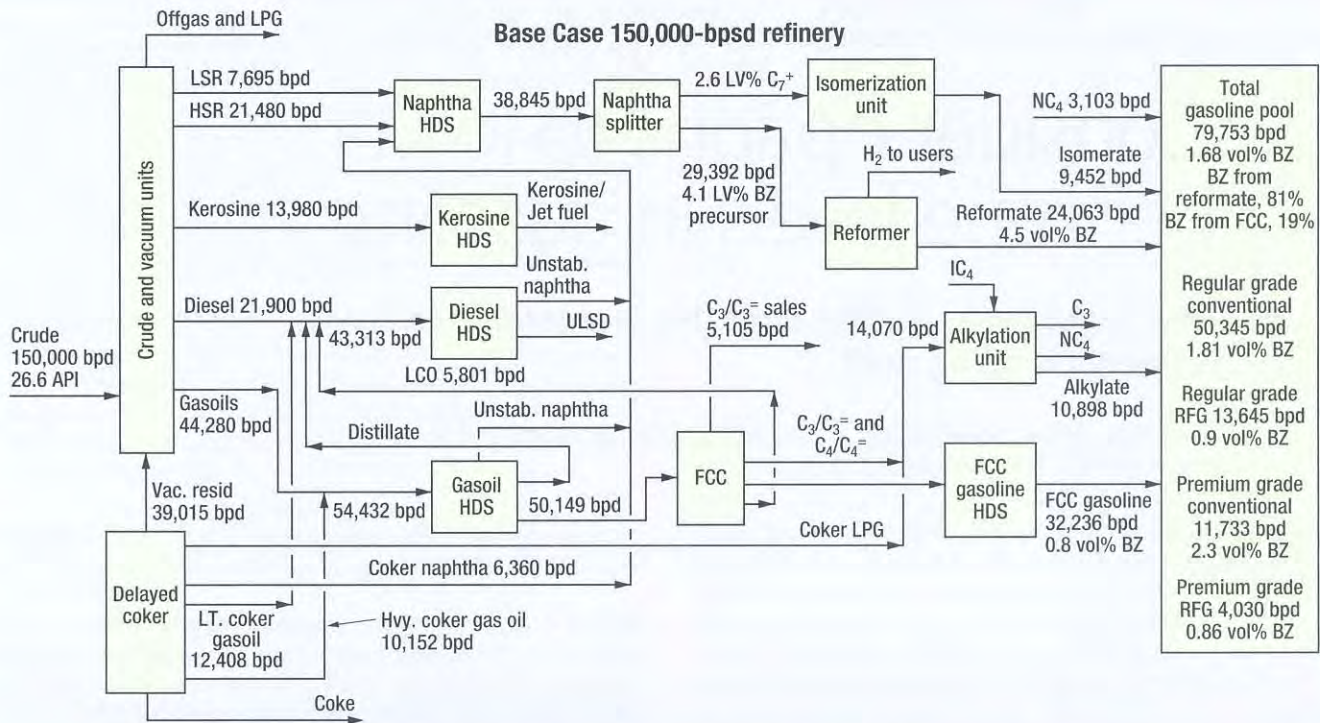


FIG. 1 Processing scheme of a 150,000-bpd refinery and the benzene content of all product and process streams.

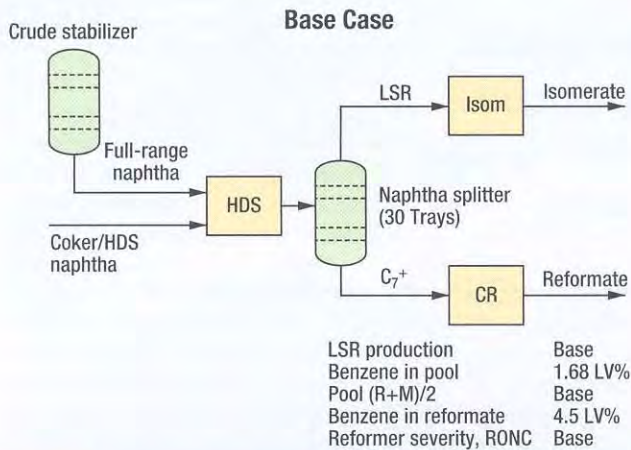


FIG. 2 The Base Case processing scheme of the naphtha unit.

TABLE 1. Benzene content and typical gasoline fraction of gasoline blendstocks

	Benzene level, vol%	Typical volume in gasoline, vol%	Typical contribution to gasoline benzene content, %
Reformate	1–6	30	70–85
FCC gasoline	0.5–1.2	35–40	10–25
Alkylate	0	10–15	–
Isomerate	0	5–10	–
Light hydrocrackate	1–3	0–4	4
Light straight-run (LSR)	0.3–4	5–10	2
Light coker naphtha	1–3	0–2	1
Natural gasoline	0.3–3	0–5	1
Butane	0	3–5	–

Hydroprocessing facilities for naphtha, kerosine, diesel, FCC feed and FCC gasoline are also included in Fig. 1. The gasoline pool benzene concentration is 1.68 vol%.

Fig. 2 shows the Base Case—naphtha processing configuration. Full-range virgin naphtha from crude distillation is combined with coker naphtha and naphtha from the diesel and gasoil hydrotreaters and processed in a naphtha hydrotreater for sulfur and nitrogen removal. The hydrotreated naphtha is fractionated in a 30-tray splitter with a reflux to distillate ratio of 1.2. The light naphtha overhead contains 2.6 vol% C₇⁺ and is processed in an isomerization unit. The splitter bottoms flows to the reformer. In the reformer, benzene is formed via several pathways:

- Dehydrogenation of cyclohexane to benzene
- Isomerization of methylcyclopentane to cyclohexane, then dehydrogenation to benzene
- Conversion of C₆ paraffins to cyclohexane, followed by dehydrogenation to benzene
- Hydrocracking (dealkylation) of heavier aromatics to benzene.

In the reformer, benzene precursors in the feed (C₆ paraffins, cyclohexane and methylcyclopentane) are partially converted to benzene. Cyclohexane conversion to benzene is essentially 100%. About half of the methylcyclopentane and 20% of the C₆ paraffins are converted to benzene. Additional benzene is formed in the reformer by hydrocracking heavier aromatics. This route to benzene formation is a function of the reformer operating pressure and reformer severity. In the Base Case example with the 30-tray naphtha splitter, the combined

benzene, cyclohexane and methylcyclopentane in the reformer feed is 4.1 vol%. The benzene content of the reformate product is 4.5 vol% benzene.

Benzene reduction options. Figs. 3 and 4 show two benzene removal options (Case 1 and 2) where a new naphtha splitter with 60 trays is installed to reduce the concentration of benzene, cyclohexane and methylcyclopentane in the reformer feed to less than 0.5 vol%. The splitter overhead C_{7+} content is held at 2.5 vol% to limit liquid yield loss in the isomerization unit. The number of trays selected for this application was based on an optimization of equipment and operating costs. More details of this evaluation are given later.

Since much of the C_6 material that was included in the Base Case reformer feed is removed by the new splitter overhead, feed to the isomerization unit is increased by about 15%.

Case 1. For Case 1 (Fig. 3), it is assumed that the existing isomerization unit is operating at capacity. Accordingly, excess LSR material is bypassed and sent directly to the gasoline pool. This reduces the reformate benzene content from 4.5 vol% to 1 vol%. The gasoline-pool benzene concentration is reduced to 0.63 vol%, which is very close to the new gasoline pool average limit.

Typically, the naphtha-fractionation approach can come very close to meeting the new benzene limit. In some cases, this processing method will be sufficient. Obviously, for the naphtha-fractionation approach, the benzene content of the FCC gasoline is very important.

Based on the recent revision to the renewable fuels standard (RFS), the US gasoline pool will average about 10 vol% ethanol. The naphtha-fractionation approach could be an acceptable strategy for many refineries. The only uncertainty is the timing of the revised RFS and the MSAT II regulations.

Since about 15% of the LSR material bypasses the isomerization unit, the overall octant pool R+M/2 is estimated to be reduced by 0.24 numbers. The pool octane reduction can be offset by increasing the reformer severity by about 1 RONC. However, this action will increase the reformate benzene content to 1.1 vol% and the gasoline pool benzene content to 0.66 vol%. Higher reformer severity may require a reformer revamp. Other options to offset the reduction in pool octane are:

- Producing less premium gasoline
- Offsetting the octane loss by blending ethanol in the finished product. This would also allow a proportionally higher benzene level in the refinery gasoline pool.

Case 2. This case (Fig. 4) is similar to Case 1, but it is assumed that the existing isomerization unit is revamped to handle the larger feed. The gasoline pool benzene content is 0.61 vol%. The benzene in the reformate is 1 vol% and pool octane is reduced by 0.14 R+M/2.

Another consideration for the naphtha fractionation approach is that individual refineries can have average gasoline pool benzene content up to 1.3 vol% as long as the average for the corporation is no greater than 0.62 vol%. This could allow a refiner to use a combination of naphtha fractionation at some sites to maintain the plant pool average below 1.3 vol% and benzene conversion or extraction technology (which can achieve pool benzene concentrations well below the limit) at other sites to satisfy the corporate average gasoline pool benzene limit.

Case 3. For this case (Fig. 5), a configuration for removing benzene from reformate is applied. A reformate splitter is installed to yield a light-reformate stream that contains essentially all of

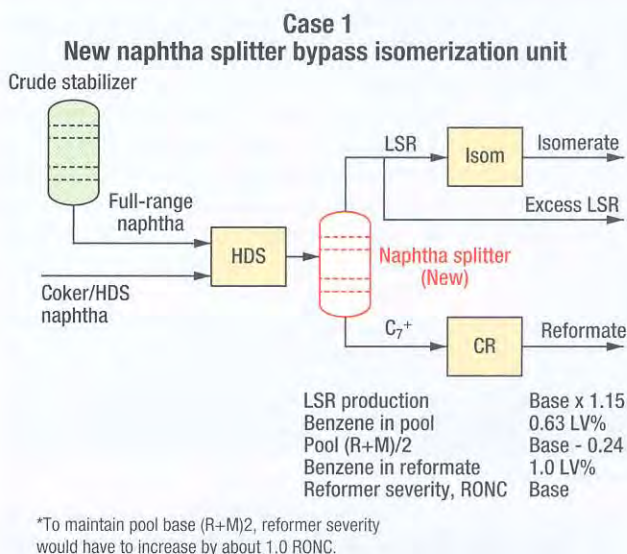


FIG. 3 Flow diagram of the benzene reduction option using a new naphtha splitter and bypassing the existing isomerization unit to send more LSR to the gasoline blending pool.

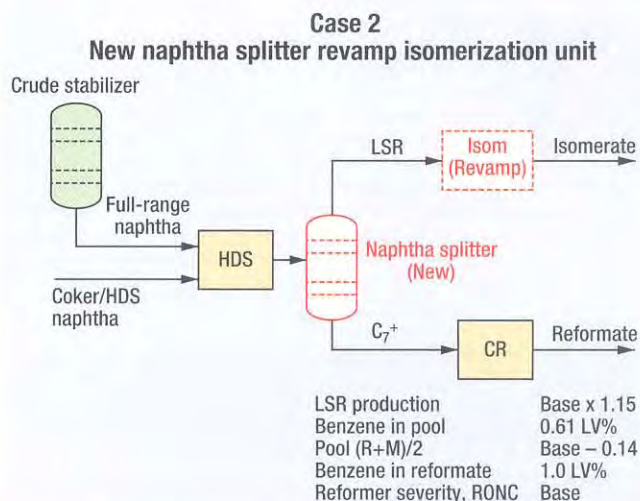


FIG. 4 Flow diagram of the benzene reduction option using a new naphtha splitter and revamping the isomerization unit to process the additional LSR material.

the benzene. The light reformate can then be processed in one of several proprietary schemes involving benzene saturation, benzene alkylation or solvent extraction.

For Case 3, a benzene saturation approach is assumed. A pool-average benzene content of 0.6 vol% is achieved by feeding about 80% of the whole reformate to the splitter and benzene saturation unit. The gasoline pool R+M/2 is reduced by 0.2. The reformate benzene content is identical to the Base Case of 4.5 vol%. The octane loss can be offset by increasing the reformer severity. Another option to recover the lost octane would be to use a combination benzene saturation/isomerization unit. Table 2 lists the results of the evaluated cases.

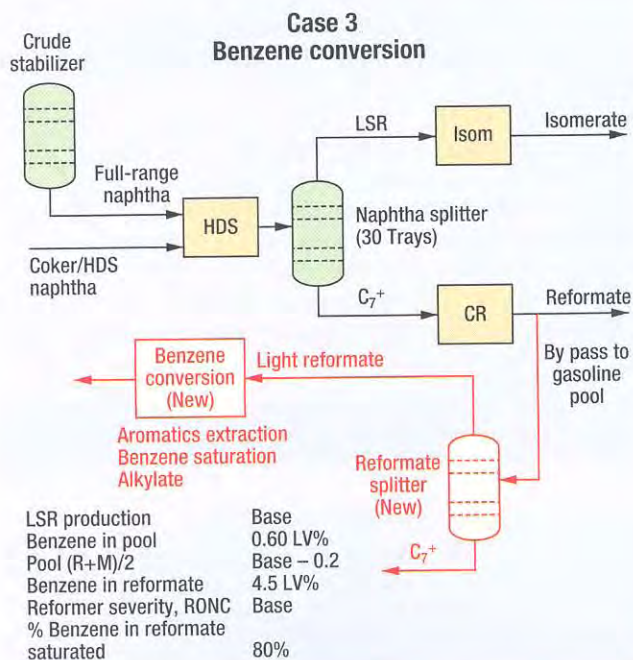


FIG. 5 Flow diagram of the benzene reduction option removing benzene from the reformat with a new reformat splitter and benzene conversion unit.

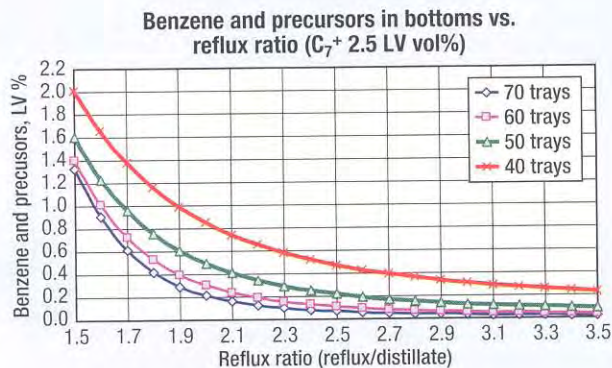


FIG. 7 The sensitivity analysis for various reflux ratios with trays used in the naphtha splitter.

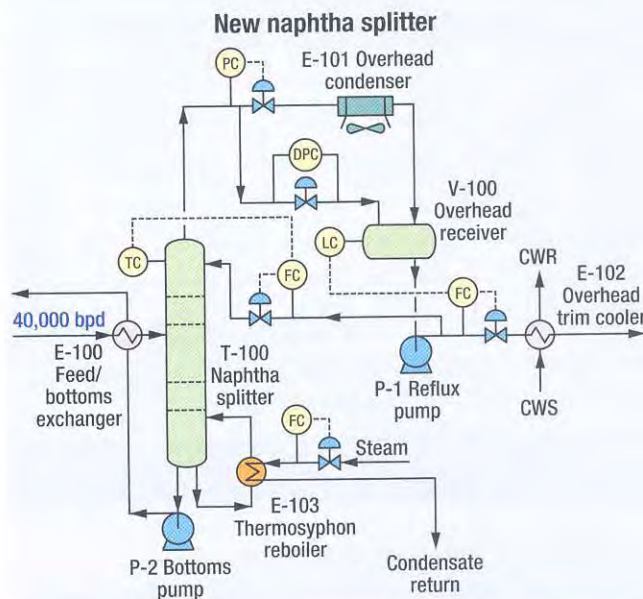


FIG. 6 Processing diagram of the new naphtha splitter of the naphtha fractionator to remove benzene.

Fractionator optimization. Benzene removal strategies that have been addressed use a new fractionator for either reformer feed or reformer product. Either of these applications requires distillation columns with a large number of trays and significant input energy to achieve desired separation. The size of the naphtha splitter for the naphtha-fractionation case was based on an optimization exercise that considered the variation of capital and operating costs relative to the number of trays within the column. The splitter system (Fig. 6) consisted of a feed/bottoms exchanger, splitter column, overhead condenser, overhead receiver, combined reflux/product pump, overhead trim cooler, steam reboiler and bottoms pumps.

The bottoms fractionation specification was set at 0.5 vol% combined benzene, cyclohexane and methyl cyclopentane. Fig. 7 shows the sensitivity of this specification to the reflux ratio for columns with 40, 50, 60 and 70 trays. The full-range naphtha feed temperature was set at 200°F. The C₇⁺ content of the overhead was set at 2.5 vol% based on the sensitivity of this specification to the reflux ratio (Fig. 8). The feed tray location was established in a similar fashion (Fig. 9). The overhead receiver temperature and pressure were set at 115°F and 5 psig. Sized equipment lists and utilities were developed for the four tower tray options already mentioned here. The price for equipment was obtained and a factored cost estimate

TABLE 2. Summary of various benzene reduction methods and benzene concentration in product streams

	Base Case	Case 1, new naphtha splitter excess LSR bypass isom unit	Case 1A, new naphtha splitter excess LSR bypass isom unit increase reformat severity	Case 2, new naphtha splitter no excess LSR bypass isom unit	Case 3, new reformat splitter and benzene saturation unit
Benzene in total gasoline, LV%	1.68	0.63	0.66	0.61	0.60
LSR production (R+M)/2	Base	Base x 1.15	Base x 1.15	Base x 1.15	Base
Benzene in reformat, LV%	4.5	1.0	1.1	1.0	4.5
Reformat RON clear	Base	Base	Base + 1.0	Base	Base
% Benzene in reformat saturated	0	0	0	0	80%

cyclohexane and methyl cyclopentane in the reformer to 0.5 vol% can reduce the benzene in reformate by about 80%, which enables the refinery gasoline pool benzene content to be very close to the MSAT II limits. The revised RFS will require blending 10 vol% ethanol into the gasoline pool; thus, the naphtha fractionation approach would be an acceptable strategy for many refineries.

An alternate, more robust compliance approach is fractionating reformer product to produce a light reformate stream containing essentially all of the benzene. This stream is processed further in a conversion facility where the benzene is converted to cyclohexane.

All of the benzene removal options addressed resulted in some total refinery gasoline-pool octane reductions. The octane loss can be offset by increasing reforming severity or reducing the volume of premium gasoline produced. The future inclusion of increased volumes of ethanol in gasoline can more than offset the octane penalties identified. **HP**

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LITERATURE CITED

- ¹ Control of Hazardous Air Pollutants from Mobile Sources, Summary for EPA 40 CFR 59, 80, 85 and 86.
- ² US EPA 420-R-07-002, Regulatory Impact Analysis, Control of Hazardous Air Pollutants from Mobile Sources: Table 6-3-1, pp. 6–17, February 2007.



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