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Cost Effective Solutions for Reduction of Benzene in Gasoline

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Cost Effective Solutions for Reduction of Benzene in Gasoline

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Introduction

In the current global quest for the production of cleaner fuels, benzene has been identified as a gasoline component that should be reduced. As a result, the Environmental Protection Agency placed a limit of 1 volume percent of benzene in reformulated gasoline (RFG) in 1995. The recently issued MSAT II regulations further reduce benzene to less than 0.62 percent in all U.S. gasoline by 2011. Europe, Canada, Australia, Japan and others have also adopted limits on benzene. Many other countries are currently in the process of reducing benzene in gasoline.

For most refiners, the reduction of benzene in RFG was easily accomplished using existing options. Many refiners simply adjusted the C₆ content of the naphtha feed to their reformer by prefractionation and produced reformat with reduced benzene content. Refiners with integrated chemical operations were able to send their light reformat to extraction facilities and move benzene into the petrochemical market. Others were also able to take advantage of this option by exporting the light reformat fraction over the fence for outside processing. Several refineries installed facilities for hydrogenation of benzene. Another possibility is reaction of propylene with benzene to produce cumene. However, this approach requires significant clean up of the impurities in refinery propylene considerably increasing the total capital cost.

The removal of benzene from the gasoline pool represents the loss of one of the highest octane components. The current program of adding ethanol to the gasoline pool will eventually make most refiners long on octane. As a result, the benzene/octane issue is not a significant factor.

The benzene reduction required by MSAT II is clearly a much larger quantity to deal with and refiners may be forced to make more substantial changes in refinery operations to achieve these levels. For many refiners, prefractionation of the reformer feed will not provide a sufficient benzene reduction. The high capital cost of benzene extraction expansions or new facilities will also not provide an attractive answer for all refiners, especially smaller refineries or those in locations remote from the petrochemical benzene users. Assuming hydrogen availability is not a problem, benzene hydrogenation may provide the answer. Even if hydrogen supply is a problem, it may well have to be addressed by the need to remove sulfur from FCC gasoline as well as other refinery products, as increased pressure to reduce sulfur emissions comes into play in the near future. The refiner who is looking down the road and making plans probably has a hydrogen plant increasing in priority.

Benzene Sources

In the typical refinery benzene comes from several sources including;

- 1) Light straight run gasoline
- 2) Reformat
- 2) Hydrocrackate
- 4) FCC gasoline
- 5) Coker gasoline

However the benzene from the reformer usually represents 50-80% of the total (Figure 1). As a result, the reformat is the natural place to focus benzene reduction. In most cases the desulfurized light straight run can be co-processed with the reformat for benzene reduction.

Reformat Is Primary Benzene Source

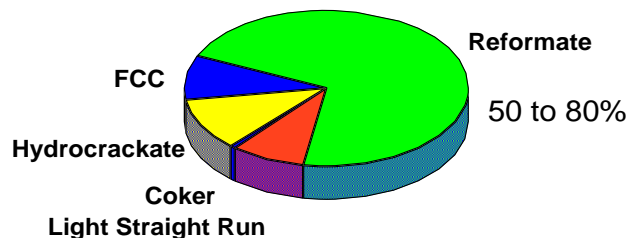


Figure 1

Conventional Benzene Saturation

The conventional approach to removing benzene from reformate is shown in Figure 2. Reformate is fractionated in a reformate splitter to take benzene and lighter components overhead. The toluene content of the light reformate fraction is limited to minimize its loss due to hydrogenation. This benzene containing fraction is sent to a hydrogenation reactor where benzene is converted to cyclohexane in a highly exothermic, high pressure,

Conventional Benzene Saturation Process Flow Diagram

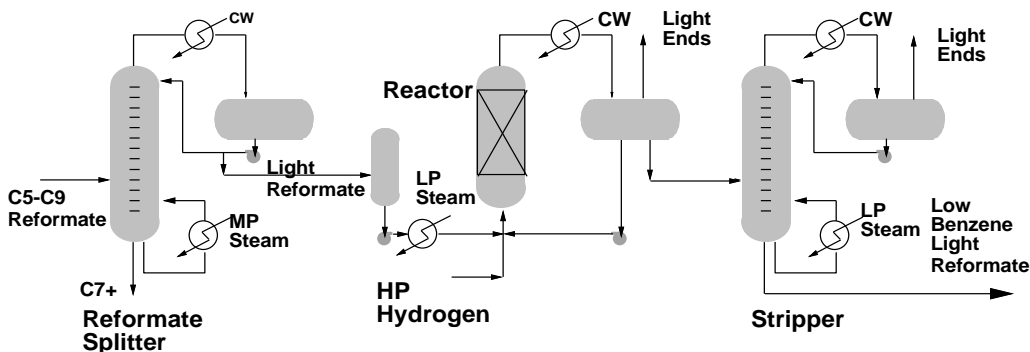


Figure 2

A cooled recycle stream is normally required to modulate reactor temperature. The reactor effluent is sent to a stripper where light ends are removed by fractionation. This approach requires many equipment items (high capital cost) and is susceptible to upsets in operation.

The CDHydro® Process

In 1994, a new process for hydrogenation was commercialized. The patented CDHydro process combines fractionation with hydrogenation. Proprietary distillation devices (CDModules®) containing catalyst are installed in the top section of the fractionation column (Figure 3). Hydrogen is introduced beneath the catalyst zone. Fractionation carries light components into the catalyst zone where the reaction with hydrogen occurs. Fractionation also sends heavy materials to the bottom. In addition, clean hydrogenated reflux continuously washes the catalyst zone. These factors combine to provide a long catalyst life.

The heat of reaction evaporates liquid and the resulting vapor is condensed in the overhead condenser to provide additional reflux. The natural temperature profile in the fractionation column results in a virtually isothermal catalyst bed rather than the temperature increase typical of conventional fixed bed reactors.

CD Hydrogenation Process Flow Diagram

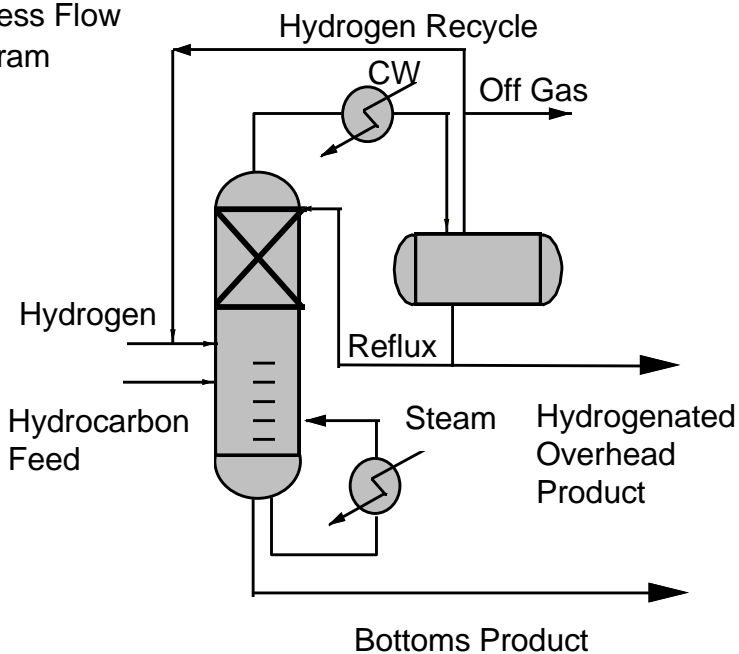


Figure 3

Light ends control can be achieved by addition of a pasteurization section at the top of the fractionation column. The overhead product is taken as a sidedraw with reduced content of hydrogen and other light ends.

The CDHydro process can operate at much lower pressure than conventional processes. Pressures for the CDHydro process are typically set by the fractionation requirements. Additionally, the elimination of a separate hydrogenation reactor and hydrogen stripper offer significant capital cost reduction relative to conventional technologies. The resulting process simplification can also reduce manpower requirements.

Another factor that is important in the design of refining units is safety. The combination of integral reaction heat removal, low operating pressure and fewer equipment items enhances the safety of the CDHydro process relative to conventional technologies.

The Benzene CDHydro Process

The CDHydro process offers significant advantages when applied to the hydrogenation of benzene. The typical process scheme is presented in Figure 4. Requirements of MSAT II can be met in a fractionation column which is similar to that required to produce the light reformate for the conventional fixed bed benzene hydrogenation process. No additional reactor system or hydrogen stripping column is required. The Benzene CDHydro column is operated to minimize the toluene in the catalyst zone. Hydrogen is added below the catalyst zone and saturation of benzene to cyclohexane in the overhead product is virtually complete. Conversion of benzene in reformate exceeding 95% has been demonstrated at 35 psig operating pressure. Most applications of the Benzene CDHydro process will be designed to achieve 70 to 99+% benzene hydrogenation at less than 100 psig operating pressure. Conventional processes require 350 to 500 psig. The Benzene CDHydro process may provide much higher levels of benzene removal than required by MSAT II in specific circumstances. In these cases refiners may want to consider using the high efficiency of the Benzene CDHydro process rather than reduce benzene in other streams or other locations. Trading of benzene reduction credits could also make this option interesting.

This first commercial installation for hydrogenation of benzene in reformate via the Benzene CDHydro process was started up in December 1995 by Texaco at its Bakersfield, California refinery. This unit was designed for a benzene conversion of 80%. Benzene conversion is controlled by the amount of hydrogen fed to the column. The column operates at a reflux drum pressure of 75 psig so that the offgas may be vented to the refinery fuel gas system. The capacity of this unit was recently increased by more than 30% by installing an advanced CDModule design with increased catalyst activity.

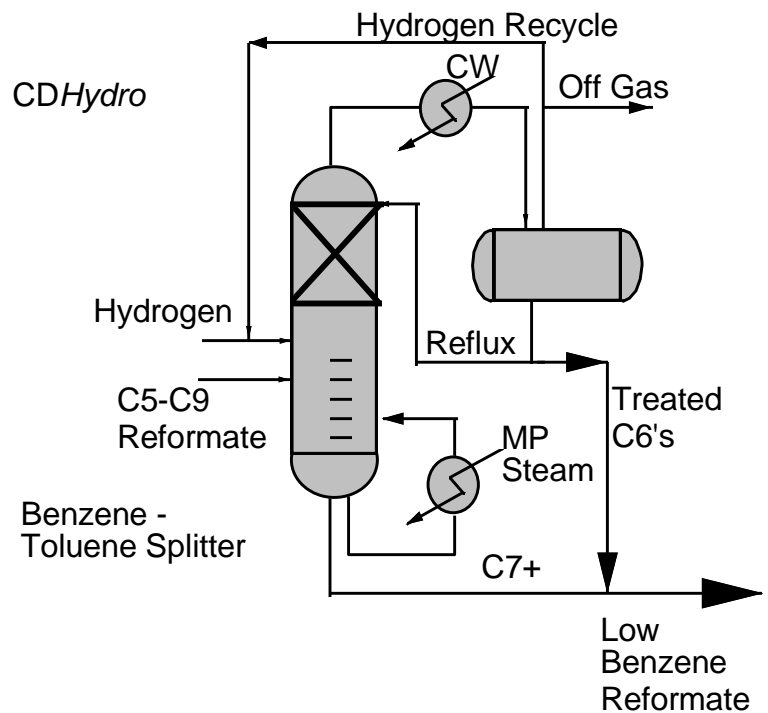


Figure 4

There were six commercial Benzene CDHydro units in operation at the end of 2005. These facilities are listed in Table 1. One more Benzene CDHydro unit is scheduled for startup in 2010.

Table 1
Benzene CDHydro Operating Units

Client	Location	Reformer	Feed Benzene %	Start-up
Texaco	Bakersfield, CA	Semi Regen	2.52	1995
Nansei Sekiyu	Okinawa, Japan	Semi Regen	5.75	1999
BP Rotterdam	Europort, Netherlands	Semi Regen	3.29	1999
Shell	Harburg, Germany	CCR	4.41	1999
ExxonMobil	Altona, Australia	Semi Regen	8.93	2005
Caltex	Lytton, Australia	CCR	10.18	2005

Alternate Configuration

In some cases the refiner may need to remove more benzene than can be accomplished by treating the reformate alone. This situation could occur if the Light Straight Run (LSR) has a high benzene content or if there are no other low benzene streams to dilute the pool benzene to the required level. Seasonal blending considerations or the periodic loss of production from key refinery units may require further benzene reduction capability to provide operating flexibility and ensure yearly average benzene limits are not exceeded. Figure 5 presents data for such a situation. This refiner needs to reduce benzene from 1.9% in the reformate plus desulfurized LSR down to 0.4% in order to meet average annual pool specifications. Even if 100% of the benzene was removed from the reformate, the LSR benzene content would keep the blended average above 0.4%. Therefore, the refiner must treat both streams for benzene removal.

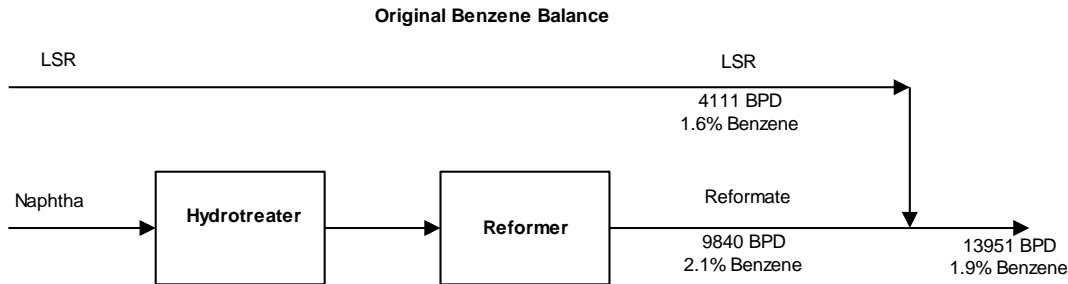


Figure 5

The following configuration (Figure 6) shows how this refiner would reduce the benzene using a conventional approach. In order to hydrogenate the benzene in the LSR, it must first be desulfurized. It may be possible to make use of the existing hydrotreating facilities for desulfurization of both the naphtha and the LSR. This also offers the opportunity to reduce the benzene precursors in the Reformer feed by fractionating them into the LSR. The resulting reformate is then fractionated to take the benzene overhead while minimizing toluene carryover. The light reformate and the LSR are combined and fed to a Benzene Saturation unit where benzene is hydrogenated to cyclohexane.

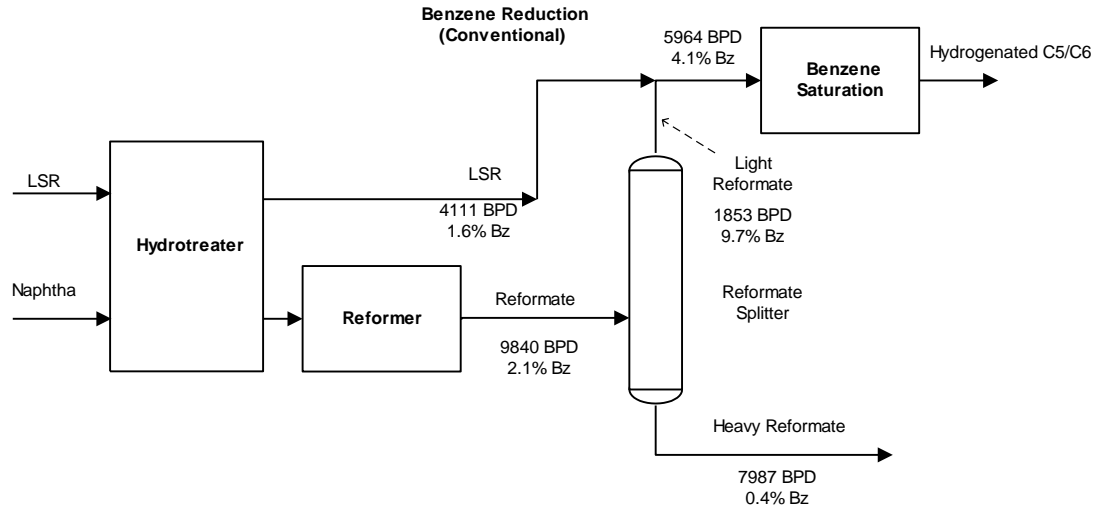


Figure 6

Figure 7 shows the simplification that can be achieved by applying *CDHydro* catalytic distillation to combine processing steps.

	Estimated Capital Costs	
	Conventional	Benzene <i>CDHydro</i> Process
Column	2.0	3.3
Reactor, Stripper, Compressor	4.0	0.0
Total	6.0	3.3

The capital cost comparison is shown above. The Benzene *CDHydro* column is more expensive than a plain column primarily because of the larger condensers and reflux system to accommodate the heat of reaction of benzene. However, elimination of a separate reactor and stripper plus make-up compressor translates to a capital cost advantage of nearly 50% for the Benzene *CDHydro* process.

Benzene *CDHydro* Process – C₅/C₆ Isomerization Integration

Advantages

When maximizing both benzene reduction and octane barrel production is the goal, refiners will likely look at processing the combined LSR and light reformate streams in a C₅/C₆ isomerization unit. Although this feedstock mixture may be isomerized without prior hydrogenation of the contained benzene, there are many instances where pretreating using the Benzene *CDHydro* process, which results in both benzene reduction and enhanced fractionation, provides economically attractive process performance advantages. These advantages include higher product octane, higher liquid volume yield, and lower expected catalyst replacement rates.

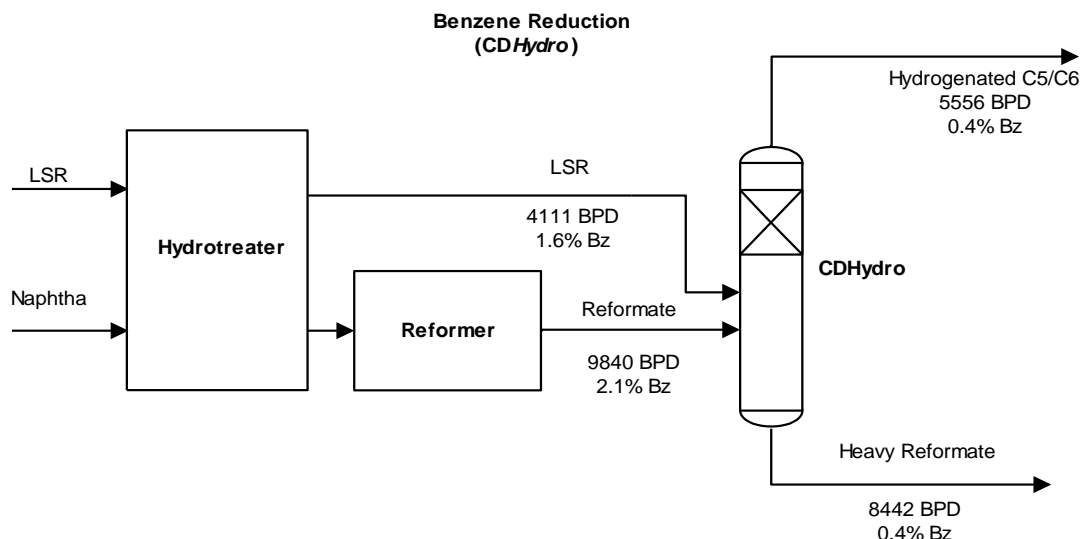


Figure 7

A number of factors contribute to these positive effects. The high heat of reaction associated with benzene hydrogenation can quickly increase the temperature in the fixed bed isomerization reactor. Because the isomerization reactions are equilibrium limited and favored by low temperature, the reduced temperature rise associated with the low benzene content feed from the Benzene CDHydro process enhances n-paraffin conversion to desired high octane isomers.

Optimized fractionation in the Benzene CDHydro column allows for a reduction in the total C₆ cyclics and C₇₊ in the feed to the isomerization unit. C₆ naphthenes tend to exclude paraffins from active catalyst sites, so their reduction also contributes to increased paraffin isomerization. C₇₊ hydrocarbons have both a diluent effect (occupying reactor volume) and partially crack increasing light ends gas make and reducing liquid product yield. Limiting their concentration, thereby, increases isomerate product yield.

Lower reactor operating temperatures and reduced cracking lowers the potential for carbon laydown, which can cause catalyst deactivation. Further, reduced reactor temperature rise allows for more freedom to raise reactor temperature in response to declining catalyst activity, thus increasing run length.

When isomerizing a typical combined LSR plus light reformate feedstock containing approximately 5% benzene and 5% C₇₊, the upstream incorporation of the Benzene CDHydro process results in an average product octane gain of 1 RONC and a corresponding 0.75%-1.5% increase in C₅₊ yield (relative to performance with non-hydrogenated feedstock). Expected annual isomerization catalyst consumption is also one-third lower with the incorporation of the Benzene CDHydro process. Resulting simple payout, based on increased octane-barrel production, is typically less than one year for the required incremental investment in the Benzene CDHydro process unit.

Conventional Processing Comparison

The conventional technology alternative to the Benzene CDHydro process for this high benzene feedstock application is to add a separate benzene hydrogenation step in front of, but integrated with, the isomerization reaction system (Figure 8). This option will increase capital cost by about 30% compared to isomerization alone.

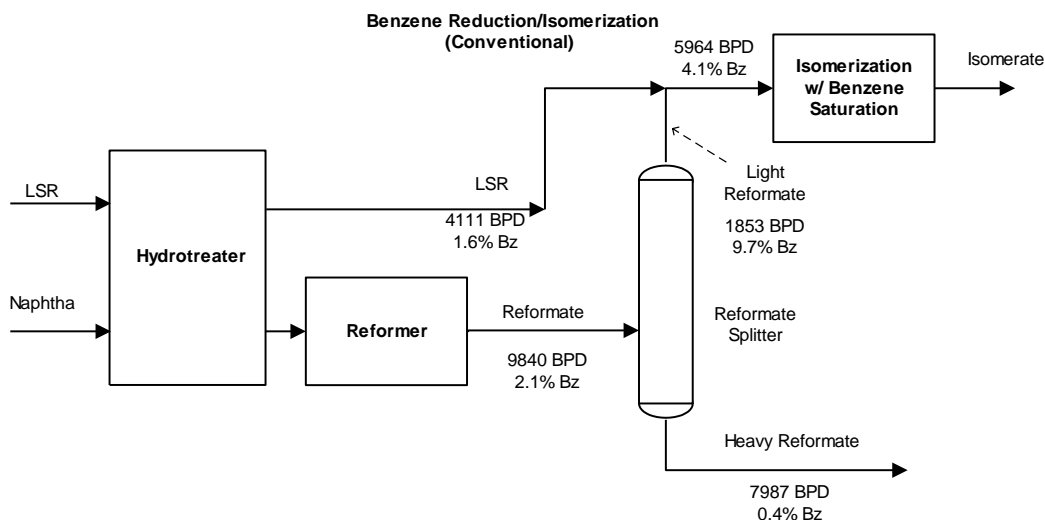


Figure 8

The use of the Benzene CDHydro process to hydrogenate benzene prior to (C_5/C_6) isomerization is shown in Figure 9. The addition of the Benzene CDHydro process to the new reformater splitter would reduce the cost of the benzene hydrogenation step by 50% compared to conventional technology.

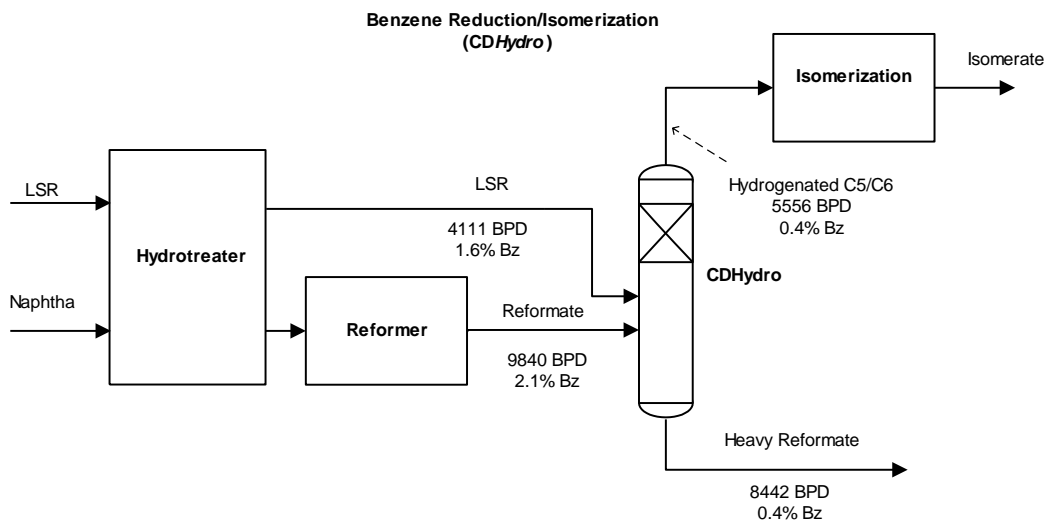


Figure 9

Further, the combined fractionation of the LSR and reformate in the Benzene CDHydro column, enhanced by simultaneous benzene saturation, allows for reduction in both the total C_6 cyclic and C_7+ content of the isomerization unit's feed. This improved fractionation is reflected in an increased heavy reformate flow rate for the Benzene CDHydro process (Figure 9) relative to the conventional processing approach (Figure 12). The corresponding benefits to isomerization unit performance, as discussed previously, contribute to higher octane isomerate and increased liquid product yield to the gasoline pool.

Conclusions

Refiners can maintain gasoline compositions with high aromatic contents by using the flexibility offered by the Complex Model and reducing benzene content for effective TOX control. The Benzene CDHydro process provides a more cost effective method of benzene reduction for the refiner than available from conventional technology.

Benzene reduction targets for MSAT II are easily met. The Benzene *CDHydro* process can provide much higher benzene removal than required by the standards, thus giving the refiner valuable options for averaging and trading credits. If benzene reduction requirements cannot be met by treating the reformat alone, the Benzene *CDHydro* process offers the capability of simultaneously processing the LSR for more complete benzene reduction.

When the octane loss associated with benzene reduction is a concern for the refiner, then isomerization of light reformat and LSR can be of interest. The hydrogenated C_5/C_6 cut from the Benzene *CDHydro* process is ideal feedstock for the isomerization unit. Its reduced benzene content coupled with optimized fractionation results in both higher yield and higher octane isomerate than can be produced from non-hydrogenated feeds. Relative to conventional hydrogenation technology in this application, the Benzene *CDHydro* process offers the dual advantages of increased isomerization unit performance benefit and significantly lower cost.

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