

# Benzene Saturation in Gasoline

## CDTECH

### Background

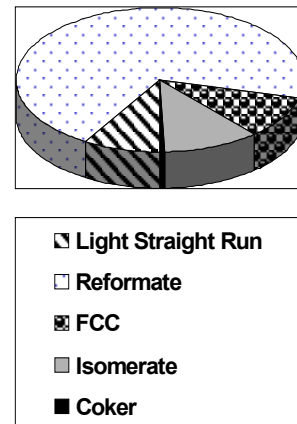
#### Fuel Specification Changes

Refinery products used for fuels are receiving increasing levels of attention. Product specifications are being scrutinized by governmental agencies, whose interests are

Table 1 - US and EU Gasoline Proposed Specifications

| <i>Specification</i> | <i>CARB</i> | <i>EU</i>       | <i>AUTOMAKERS</i> |
|----------------------|-------------|-----------------|-------------------|
| Max Level            |             | 2005            |                   |
| Sulfur, ppm wt       | 40          | 50              | 10                |
| Aromatics, vol%      | 25          | 35              | 35                |
| Olefins, vol%        | 6           | 18 - AO-II      | 10                |
| Benzene, vol%        | 1           | 1.0             | 1                 |
| Summer RVP, kpa      | 48(7)       | 60(8.7) - AO-II | 60                |
| Lead                 | 0           | 0               | 0                 |
| Oxygen, wt%          | 2.2         | 2.7 - AO-II     | 2.7               |
| E100C, min vol%      | 50@210F     | 46 - AO-II      | 50                |
| E150C, min vol%      | 90@310F     | 75 - AO-II      |                   |
| E180C, min vol%      |             |                 | 90                |
| EP, Deg C,max        |             |                 | 195(383F)         |
| DI                   |             |                 | 570               |

Figure 1- Benzene in Gasoline



decreased emissions from mobile and stationary sources, and by the industries that produce the engines and vehicles that utilize these fuels (Table 1).

The European Union, followed closely by the United States, is implementing significant changes in gasoline specifications. CARB imposed dramatic changes in the early 1990's, Automakers worldwide have proposed a set of limitations for gasoline and diesel to allow them to manufacture vehicles which will produce significantly lower emissions over their lifetime. This paper addresses processes that offer the refiner cost effective options for reducing benzene levels in the gasoline pool.

## **Source of Benzene**

In the typical refinery benzene comes from several sources (Figure 1) however, the benzene from the reformer usually represents 50-80% of the total. FCC gasoline is only a minor contributor to benzene in the gasoline pool. As a result, reformate is the natural place to focus benzene reduction.

## **Chemistry of Benzene Saturation**

### **Benzene Hydrogenation**

The primary reaction is the saturation of Benzene. The primary product is cyclohexane (CH). There are small amounts of cyclohexadiene and cyclohexene under some conditions, but these are not significant for fuel products. Benzene saturation represents a considerable loss of octane. The pure component octane of CH more than 20 numbers less than benzene.

### **Cyclohexane Isomerization**

A beneficial side reaction of benzene saturation is the isomerization of cyclohexane to methylcyclohexane (MCP). This occurs at elevated temperatures with an acidic catalyst. The pure component octane of MCP is 8 numbers higher than CH.

### **Straight Chain Paraffin Isomerization**

The isomerization of normal pentane (nC5) and normal hexane (nC6) to isopentane (iC5) and isohexane (iC6) increases the octane of the stream. This occurs at elevated temperatures with an acidic catalyst. The pure component octane of iC5 is 35 numbers higher than nC5, while iC6 exceeds nC6 by more than 50 numbers.

### **Benzene Mitigation Examples**

The following examples are based on 50,000 bpd of straight run naphtha containing 1.0% benzene. The base case assumes that the feed is deisohexanized with 0.5% benzene in the distillate and the reformer operates with 80% gasoline yield, 1000 scf/bbl hydrogen yield and 3.0% benzene in the reformate. If the light straight run (LSR) naphtha is sent to an isomerization unit, there are additional considerations relative to its benzene content. Any benzene in the isom unit feed is saturated in

the isom reactor. The heat of reaction increases the temperature which shifts the reaction equilibrium, thus limiting the amount of isomerization. The resulting isomerate has a lower octane number than that from LSR with low benzene content.

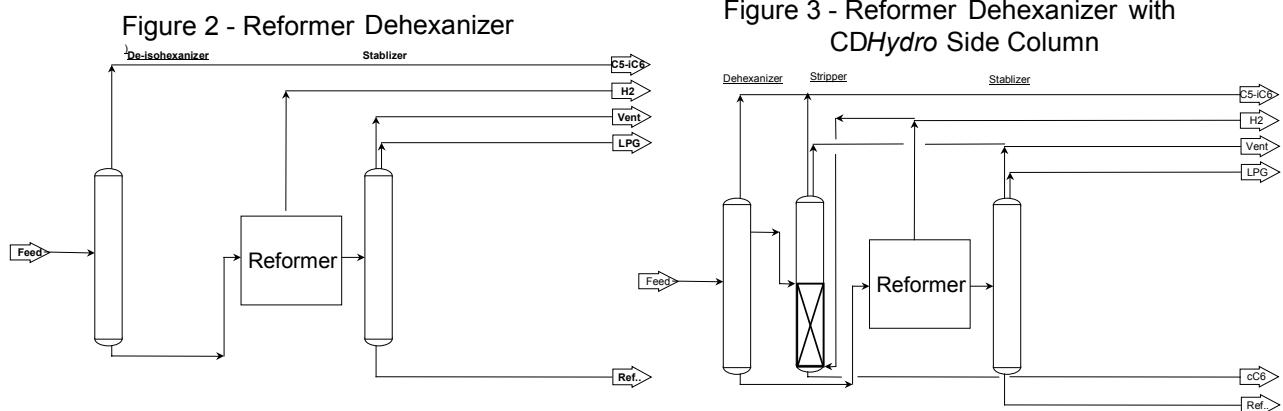
Table 2 - Naphtha Comparisons

|                       | Straight Run Naphtha                           | Coker Naphtha                   | Heavy Hydrocrackate       | Light Hydrocrackate | Hydrocracker Main Frac Tops            |
|-----------------------|--|---------------------------------|---------------------------|---------------------|--|
| Aromatics             | low  | high                            | 15%                       | < 15%               | < 15%                                  |
| Olefins               | nil  | high                            | very low                  | very low            | very low                               |
| Benzene               | 0.5 – 1%                                       | 2 – 4%                          | nil                       | 2 – 4%              | 2 – 4%                                 |
| Sulfur                | 500 – 2000 ppm                                 | typ. 1%                         | < 5ppm                    | < 15ppm             | < 15ppm                                |
| Nitrogen              | low  | high                            | nil                       | nil                 | nil                                    |
| Processing            | Debut<br>DIH<br>NHT<br>Reformer                | Debut<br>DIH<br>NHT<br>Reformer | NHT if high S<br>Reformer | DIH<br>Reformer     | Debut<br>DIH<br>Reformer               |
| Benzene from Reformer | 2 – 5% full<br>5 – 10% light<br>0.3 – 1% heavy | 2 – 5% full                     | 0.3 – 1%                  | 13 – 18%            | 5 – 10%<br>4 – 6% if highly paraffinic |

## Reformer Feed Dehexanizer

Removing the benzene precursors from the reformer feed (Figure 2) nearly eliminates the benzene in the reformat (minimum is generally 0.3 %wt and ranges up to 1.0% depending on conditions). There is however a sharp increase in the concentration of benzene in the light gasoline (former DIH tops) from 0.5% to 5.0%. The higher benzene content of some crudes can result in dehexanizer overheads with as much as 8 to 10% benzene. There is also a shift in yields. The dehexanizer tops rate increases by 1/3 (from 15% to 20% of naphtha) with a corresponding decrease in reformer feed of 6%. There is a loss of hydrogen yield of up to 10 %, as the entire hydrogen loss cannot be made up with increasing reformer severity. This does, however, reduce the combined benzene in these two streams by 40%.

## Reformer Feed Dehexanizer with Side Column



This option (Figure 3) still removes the benzene precursors from the reformer feed (Figure 2) and nearly eliminates the benzene in the reformat (as described above). The tops composition is unchanged. The side draw contains most of the benzene and precursors.

The benzene is saturated in the CD portion of the side column. The combined distillate from the dehexanizer and side column is essentially the same as the previous DIH tops. The bottoms of the dehexanizer is the same in this case as

above. The new C6 product contains less than 0.5% benzene. This reduces the combined benzene in these three streams by 80% compared to the original two streams. There is a loss of hydrogen yield by chemical consumption of 38 scf/bbl of Straight Run Naphtha in addition to the above yield loss.

This option also minimizes the benzene content of the LSR. If the resulting LSR is isomerized, the low benzene content will maximize the octane produced in the isom unit.

### Reformate Fractionation

The reformate can be fractionated to produce a benzene concentrate (Figure 4) . For a single, three-product splitter column, the concentrate is approximately 10-15% of the full range reformate and recovers ca 90% of the benzene, more or less depending on the column design. This concentrate can be further processed in a benzene extraction or recovery unit.

Figure 4 - Reformate Fractionation

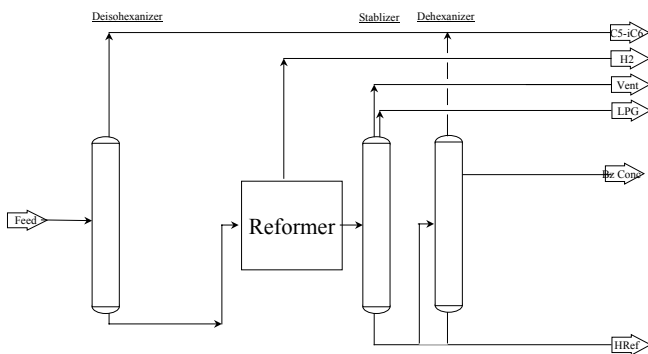
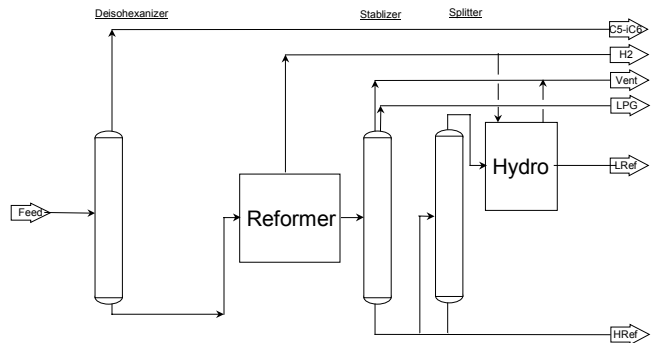


Figure 5 - Reformate Splitter with Saturation



## **Reformate Splitter with Saturation**

The reformate can be split into two fractions with the bottoms containing, say, 0.2% benzene and the tops free of toluene. Conventionally, the distillate is processed in a high pressure, fixed bed benzene saturation unit. (Figure 5) CD Hydro technology saturates benzene within the splitter column itself (Figure 6). Both the fixed bed and CD versions of the technology convert the benzene to cyclohexane.

An alternative configuration is a low pressure existing reformate splitter with a side column incorporating CD technology (Figure 7). Advantages of this configuration include: less CD packing and a higher pressure vent

In all cases, the benzene reduction can be controlled in a wide range, but is assumed to be near 90% in all cases. The loss of hydrogen yield by chemical consumption is 69 scf/bbl of Straight Run Naphtha. Vent losses vary with local conditions.

A further refinement of the above splitter scheme is to modify the reformate stabilizer upstream to enable a benzene/toluene 'heartcut,' to be drawn. The heartcut is then routed to a reformate splitter; the splitter in this case is smaller and less costly because of the reduced hydrocarbon throughputs.

## **Comparison of Alternatives**

### **Reformer Feed Dehexanizers**

The biggest impact of feed dehexanizing is the yield of gasoline and hydrogen. The actual yields depend on how the severity and the reformer feed is adjusted. If there is no change, the combined gasoline production from the DIH and the reformer increases by 1% but the hydrogen yield decreases by 10% and there is a slight reduction in the octane value. The only real cost of this alternative is the loss of hydrogen production from the reformer. There is little or no capital cost required for changing a deisohexanizer into a dehexanizer.

The addition of a side column for benzene saturation doubles the benzene reduction. The major operating costs are hydrogen, octane loss and catalyst cost. There is potentially a net energy credit from the high temperature condenser.

### Reformate Fractionation

Distillation of the Reformate to produce a benzene concentrate followed by benzene extraction requires the largest capital expenditure and highest energy cost of all alternatives. The value of benzene produced does not cover the operating costs.

### Reformate Splitter with Saturation

There are three variations of benzene saturation processes. All can achieve the same benzene removal. All three have the same total cost if compared on a grass-roots basis with variations in capital, energy and catalyst costs. Hydrogen cost and octane loss dominate the operating cost.

Table 3 - Comparison of Options

|                                   |      |           |           |           |           |         |          |
|-----------------------------------|------|-----------|-----------|-----------|-----------|---------|----------|
| Octane-bbl lost (octane * kbpd)   |      | 8.6       | 17.6      |           | 18.6      | 18.6    | 18.6     |
| Hydrogen Yield loss (scf/bbl)     |      | 68        | 68        |           |           |         |          |
| H2 required (scf/bbl)             |      |           | 41        |           | 84        | 84      | 84       |
| benzene concentrate               |      |           |           | 3.4       |           |         |          |
| % bz                              |      |           |           | 15%       |           |         |          |
| Separation energy (MM BTU/hr)     |      | 3.1       | 3.1       | 96        | 25.0      | 35.7    | 25.0     |
| Steam Generation (MM BTU/hr)      |      |           | 6.5       |           |           |         | 13.5     |
| packing volume cf or lb           |      |           | 338.3     |           | 363       | 1,751   | 700      |
| New equipment count               |      |           | 5         | 7         | 10        | 5       | 10       |
| Capital Cost (,000) incl 25% osbl | \$ - | \$ -      | \$2,000   | \$12,500  | \$ 11,250 | \$8,750 | \$10,000 |
| Yields Cost (Gain) \$,000/yr      |      | (\$2,923) | (\$2,136) | (\$2,123) | \$1,630   | \$1,630 | \$1,630  |
| Hydrogen cost (\$,000/yr)         |      | \$3,570   | \$5,701   | \$ -      | \$4,412   | \$4,412 | \$4,412  |
| Energy cost (\$,000/yr)           |      | \$79      | (\$3)     | \$2,410   | \$630     | \$900   | \$460    |
| Catalyst / packing cost           |      |           | \$237     |           | \$102     | \$350   | \$140    |
| Maintenance (4% of Cap)           |      |           | \$80      | \$500     | \$450     | \$350   | \$400    |
| Total Operating Cost (\$,000/yr)  |      | \$725     | \$3,879   | \$787     | \$7,224   | \$7,642 | \$7,042  |
| Capex (x% per year)               | 27%  |           | \$533     | \$3,332   | \$2,999   | \$2,332 | \$2,666  |
| Total Cost (\$,000 per year)      |      | \$725     | \$4,412   | \$4,119   | \$10,223  | \$9,974 | \$9,708  |
| cost per bz bbl                   |      | \$5       | \$14      | \$12      | \$31      | \$31    | \$30     |

The conventional system employs a low pressure splitter and a high pressure feed pump, reactor, air cooling, high pressure flash drum and recirculating pump. The estimated cost of the hydrotreater is \$3,000,000 for 6,800 bpd of light reformate, in addition to the cost of a low pressure stripper.

A higher pressure CD splitter (ca 75 psig) cost 15% more to build than a low pressure splitter due to the larger reboiler and condenser capacity. This assumes a fired reboiler is not required. This however eliminates the additional equipment associated with the conventional hydrotreater for capital savings of \$2,000,000. This is partially offset in additional operating costs of \$410,000 per year due to higher energy requirements and higher catalyst costs.

The option of a CD side column for saturation has estimated capital savings of \$1,000,000 compared to the conventional high pressure hydrotreater. This is expected due to the lower CD operating pressure and 4 of 5 pieces of equipment being smaller than conventional. The operating costs are also lower by \$170,000 per year mainly due to an energy credit on the CD column condenser (ca 350°F) with all other things being equal.

### **Economic Case Comparison**

Table 3 compares the Capital, operating and yield changes for the cases discussed above. The most economic case for a refiner will depend on the level of benzene that must be removed from the reformate, if any, to reduce the blended gasoline benzene level below 1.0%. The gasoline grade which has the highest concentration of reformate will likely be controlling, unless FCC gasoline is also a significant contributor to another reformate containing grade. Refiners who are extracting benzene already will likely not have to make any change. However, they may want to provide a minimal benzene manufacture option for periods when benzene extraction is not economically attractive. Some saturation may be required in that option.

If a refiner requires up to about 40% reduction in his reformate benzene, a simple shift in reformer feed fractionation is the most likely option. The reduction in

hydrogen production would require some alternative sourcing, but can likely be justified relative to higher capital alternatives. If the refiner already has a C<sub>5</sub>/C<sub>6</sub> isom unit fed from the dehexanizer top, additional benzene will be saturated in that unit, and nothing further will likely be required although isomerate octane will be reduced. Generally about 80% reduction can be achieved by adding a CDHydro side stripper reactor to a side draw from the reformer feed dehexanizer.

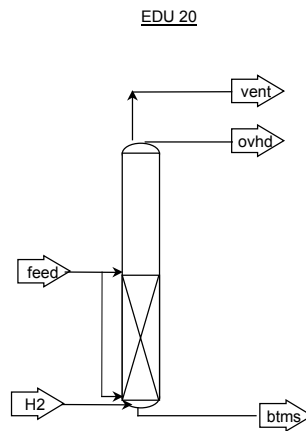
If after all this there is still too much benzene in the reformate, reformer product must be treated. The three options discussed are comparable in cost, unless a naphtha splitter is already in place. Retrofit of that column to add a CDHydro side stripper reactor provides a clear economic advantage over a fixed bed unit.

Each refiner must determine what the benzene reduction requirements is. After that we can provide guidance on the most economic route to accomplish that reduction. CDHydro is a low cost leader in this application.

### Development of the Downflow System

A series of tests were conducted to establish a new range of operation for aromatics saturation. This included the effect of operating pressure, reboiler rate and location of the catalyst relative to feed. The piloted scheme is shown in Figure 8.

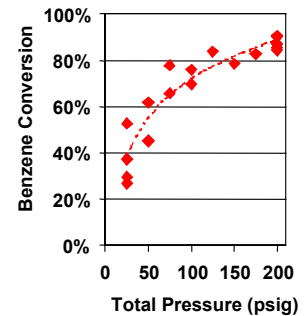
Figure 8 -Downflow Benzene Saturation



## Operating Pressure

Increasing the operating pressure has three effects on the reaction kinetics: increasing the temperature, increasing the hydrogen concentration in the liquid phase and increasing the hydrogen partial pressure. All of these effects are positive and have and have an expected positive overall effect (Figure 9). This higher pressure and temperature however has a strong negative effect on the distillation. This higher operating pressure and temperature is impractical in a reformat splitter result in elevated bottoms temperature and an increase in reflux.

Figure 9 - Effect of Pressure



## Reboil

Increasing reboil increases vapor / liquid traffic. This improves contacting which improves mass transfer. This effect is offset by a reduction in H<sub>2</sub> concentration, vapor residence time, liquid residence time and the concentration of aromatics. The overall effect is negative (Figure 10). This would suggest that the best results would be obtained by the minimum reboiler rate. Tests have demonstrated continuous, stable operation in the 3" CDU at over 90% conversion with the reboiler shut off.

Figure 10 - Effect of Reboil

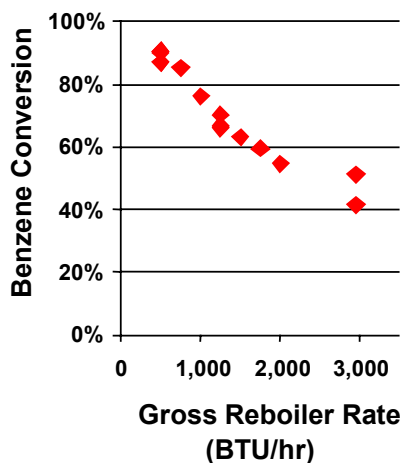
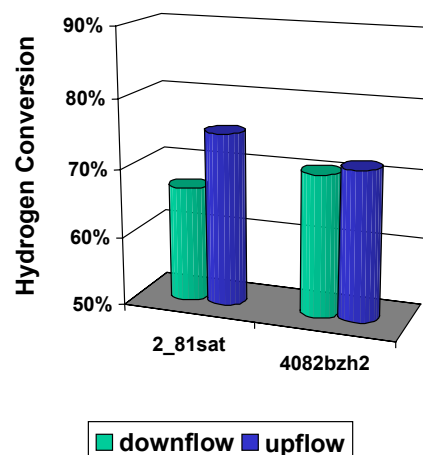


Figure 11 - Effect of Feed Location



## **Feed Location**

Location of the catalyst packing relative to the feed location is critical when the product has a different relative volatility than the reactants (MTBE, TAME, MAPD vs propylene, etc). In the case of benzene hydrogenation, there is no clear choice. The normal boiling point of cyclohexane is only 1.1°F higher than benzene. Tests with benzene and cyclohexane only show there is no significant difference whether the feed is above the catalyst or below the catalyst (Figure 11). This demonstrates that downflow is as effective as upflow for benzene saturation.

## **Conclusions**

CDTECH offers three different *CDHydro* processes for benzene reduction in gasoline:

- A side column on the naphtha deisohexanizer to eliminate straight run benzene while tailoring the feed to the reformer.
- A reformate splitter with integral benzene saturation
- A side column on a conventional reformate splitter. This reduces the energy and catalyst cost compared to the single column approach.

These three processes offer the refiner cost effective options for reducing benzene levels in the gasoline pool. These options offer reduced capital cost and/or operating cost compared to the conventional options of simple feed tailoring, benzene fractionation/extraction or fixed bed hydrotreater.