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KEEPING IT CLEAN WITHOUT AFFECTING QUALITY

Efforts to minimise air pollution have already led to significant reduction of sulfur in motor fuels in the US, Canada, the EU and several smaller geographic areas. This move is expected to continue and gradually be achieved in the rest of the world by 2020. Untreated gasoline may contain as high as 1000 ppm sulfur. The reduction is usually applied in multiple steps with a final goal of 10 - 30 ppm sulfur.

The major contributor of sulfur in the gasoline pool is the gasoline produced by the refinery fluid catalytic cracking (FCC) unit. The sulfur in this stream may exceed 2000 ppm when produced from high sulfur crudes and may make up from 10 - 80% of the refinery gasoline pool. Some refiners may process the FCC feed in a pretreatment unit, resulting in an FCC gasoline sulfur content of 10 - 100 ppm. This stream may not require further treatment in order to achieve the refinery gasoline pool sulfur specification.

Refiners who do not pretreat the FCC feed will need a post treater on the FCC gasoline product to reduce its sulfur content. Some commercially proven hydrodesulfurisation processes can effectively reduce the sulfur to the required level; however, there is normally a loss of octane in the treated product due to the saturation of olefins inherent to the hydrodesulfurisation processes. The octane loss is a function of the feed sulfur and olefin content as well as the performance of the particular desulfurisation technology.

One option that enables the refiner to offset the octane loss in the FCC gasoline is to produce ethers from the contained light olefins. This article describes the CDTECH technologies that have been developed and commercially applied for this purpose.

Properties of FCC gasoline

Figure 1 is a plot of the concentrations of total sulfur, mercaptan sulfur (RSH), and olefins (measured via bromine number) as a function of the boiling point of the FCC gasoline. In the light end of the gasoline, the olefin concentration is high and the total sulfur concentration is relatively low. Nearly all the total sulfur is in the form of RSH. As the boiling point increases, the sulfur concentration begins to increase quite significantly while the RSH concentration actually declines. In the heaviest end, most of the sulfur is

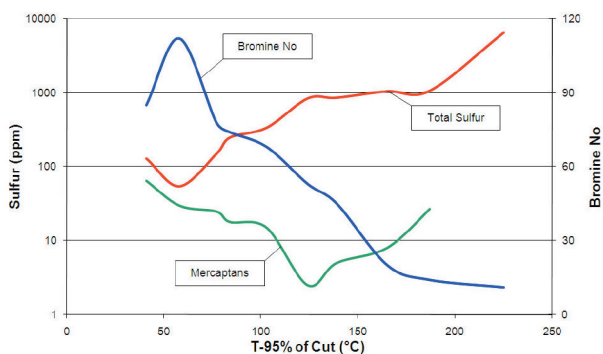


Figure 1. Concentration profiles of total sulfur, mercaptans and olefins (as bromine number) in FCC gasoline.

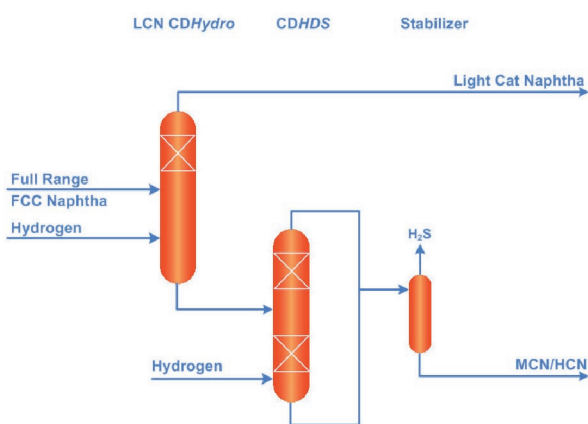


Figure 2. CDTECH's approach for minimum octane loss.

contained in compounds such as thiophene, methyl thiophene, etc. Conversely, the olefin concentration profile follows the opposite trend: the lighter end of the gasoline is olefin rich while the heavier end contains very little olefin.

The data in Figure 1 illustrates the challenge involved in treating the light end of the gasoline through to the heavy end. To meet a 10 ppm sulfur spec, the light cut requires only 90% sulfur conversion, the middle cut (near 135 °C) requires 99% conversion, while the heaviest cut requires 99.8% sulfur conversion.

Olefins provide a significant contribution to the octane rating of FCC gasoline. The preservation of olefins is vital to reducing hydrogen consumption and minimising octane loss. Olefin saturation, although inevitable in a hydrodesulfurisation process, is minimised when the sulfur conversion is minimised. With this in mind, an ideal desulfurisation process would provide an environment where the highest severity is applied only to the heavy fraction of the gasoline, which has high sulfur and low olefin concentrations. The olefins in the heavy fraction also have lower octane than the olefins in the light fraction. The reaction severity would be decreased for the lighter fractions, which have lower sulfur and higher olefin concentrations. Treating the lighter fraction at lower severity limits the saturation of valuable olefins in this olefin rich region.

Process overview

CDTECH has developed a selective treatment method for the full range FCC gasoline that optimises the severity for treating different cuts of gasoline to maximise sulfur removal while minimising olefin loss. As shown in Figure 2, the first step is to treat the lightest fraction of the gasoline in a light cat naphtha (LCN) CDHydro[®] unit where the RSH is non-destructively removed. The LCN CDHydro unit is not a hydrodesulfurisation step. It operates at very mild conditions, resulting in no measurable olefin loss.

Part of the rectification section of the LCN CDHydro column contains catalyst packed in a distillation structure. The rest of the

Table 1. Equilibrium conversion to TAME/TAEE

| Reaction | Equilibrium conversion | CDTECH conversion |
|-----------------------|------------------------|-------------------|
| C5 isoolefins to TAME | 70 | 96 |
| C5 isoolefins to TAEE | 50 | 95 |

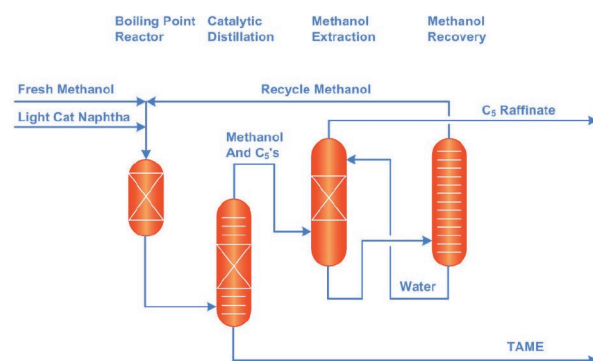


Figure 3. CDTECH unit process flow diagram.

column contains conventional distillation trays. The LCN CDHydro unit works by performing an addition reaction between the RSH and the contained diolefins over the catalyst to form a heavier sulfide (RSR). The heavy sulfide goes to the bottom of the LCN CDHydro column and exits with the bottom product.

The light product (LCN) from the LCN CDHydro column has very low RSH, a very high olefin concentration, a high octane rating, and a relatively high Reid vapour pressure (RVP). Some refiners choose to isolate this fraction in order to increase the number of degrees of freedom in the blending operation.

The LCN CDHydro column bottoms go to the CDHDS column. This is the hydrodesulfurisation step that converts the sulfur in the gasoline to H₂S. The CDHDS column also contains a

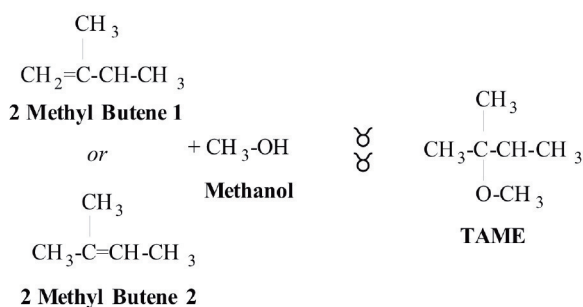


Figure 4. Isoamylene etherification to TAME.

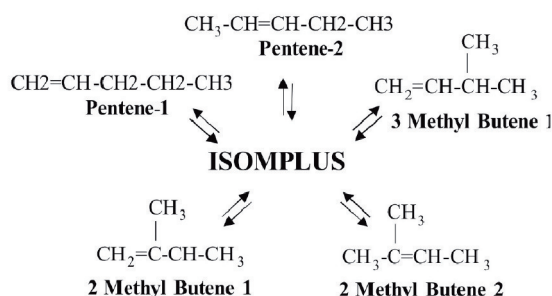


Figure 5. Olefin skeletal isomerisation.

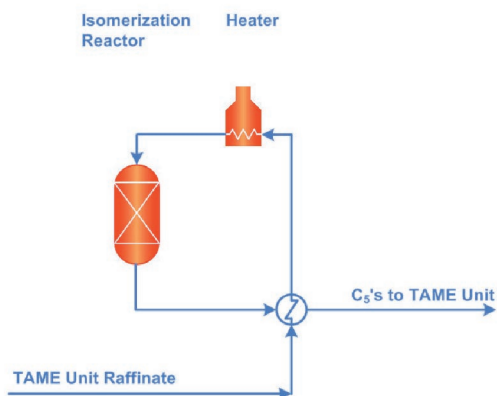


Figure 6. C5 ISOMPLUS unit process flow diagram.

hydrodesulfurisation catalyst packed in a distillation structure. Since the process is based on distillation, the catalyst structure below the feed point operates at much higher temperatures than the catalyst structure above the feed point. This has the effect of increasing the reaction severity on the heavy portion of the gasoline, where the sulfur conversion requirement is the highest and the olefin content is the lowest. Simultaneously, the medium cat naphtha (MCN), which contains higher olefin levels and less refractory sulfur compounds, goes up the column where the conditions are less severe than at the bottom. Thus, the reaction conditions in the CDHDS unit are ideally suited to the stated goals of preserving olefins and minimising octane loss.

Since the CDHDS unit performs distillation, there is an opportunity to isolate two additional FCC gasoline fractions to increase blending flexibility and control the end point of the product. The CDHDS column distillate product (MCN) makes an ideal low end point blend stock for the gasoline pool.

Technologies for octane enhancement

Etherification

The company has experience in etherification for the production of methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), and tertiary amyl ethyl ether (TAEE). These processes are based on catalytic distillation and have been used in over 80 units worldwide.

These processes are based on a two step reactor design, consisting of a boiling point fixed bed reactor followed by final conversion in a catalytic distillation column (Figure 3). The process utilises an acidic ion exchange resin catalyst in both the fixed bed reactor and the proprietary catalytic distillation structures.

The boiling point reactor is designed so that liquid is allowed to reach its boiling point by absorbing the heat of reaction, after which a limited amount of vaporisation takes place, thereby maintaining precise temperature control. The maximum temperature is adjusted by setting the total system pressure. Since the reacting liquid mixture temperature cannot exceed the boiling temperature, control is far superior to those systems in which heat must be transferred by convection or conduction. This design retains the heat of reaction as latent heat, reducing heat input requirements for the ensuing fractionation. Reactor effluent is cooled by condensation rather than by convection, resulting in the use of smaller size equipment.

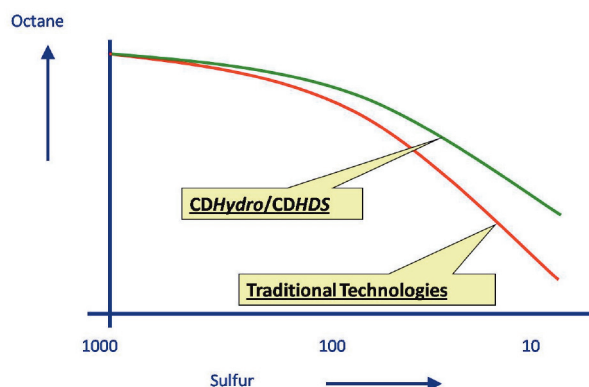


Figure 7. Octane versus sulfur reduction for desulfurisation processes.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. It allows a high conversion of isoolefins (exceeding fixed bed limitations) to be achieved simply and economically. By using distillation to separate the product from the reactants, the equilibrium limitation is exceeded and higher conversion of isobutylene is achieved. Catalytic distillation also takes advantage of improved kinetics through increased temperature without penalising equilibrium conversion.

Figure 4 shows the chemical reaction for the production of TAME and TAE. The equilibrium conversions for the production of TAME and TAE are shown in Table 1. In general, C₅ isoolefins are routed to an etherification unit where very high conversion to TAME is achieved. The bioether TAE can be produced by substituting methanol with bioethanol.

Specifically for C₅ isoolefins, the single pass conversion to ethers is very low, and a substantial benefit can be achieved by using catalytic distillation.

Other processes make use of a side draw from the fractionator (containing unconverted isoolefins and ethanol) that is recycled back to the etherification reactors. With this recycle, the overall conversion of isoolefins can be increased; however, this additional conversion is relatively low compared to that achieved by employing catalytic distillation. The recycle process consumes significantly more utilities due to the large recycle stream, resulting in utilities costs that are two to three times higher. The high recycle rate not only results in higher operating costs, but also in higher investment costs.

Skeletal isomerisation

Additional ethers production can be achieved by producing isoolefins from the normal olefins that otherwise cannot be reacted to produce ethers. CDTECH offers ISOMPLUS® technology specifically for skeletal isomerisation of normal C₅ olefins (e.g. pentene-1 or pentene-2) to C₅ isoolefins, such as the various methyl butenes (Figure 5).

Catalyst specifically developed for this service provides near equilibrium conversion of normal pentenes to C₅ isoolefins at high selectivity. The process configuration is simple (Figure 6) and

moderate process conditions result in low capital and operating costs.

The C₅ raffinate from the TAME unit, which is rich in normal pentenes, is vaporised and superheated prior to entering the skeletal isomerisation reactor. The hydrocarbon feed does not require steam or other diluents, nor the addition of catalyst activation agents to promote the reaction. The vapour stream passes through the fixed bed reactor, where the conversion takes place.

In the C₅ ISOMPLUS process, up to 66% of the normal pentenes are converted at greater than 95% selectivity to isoamylenes. The reactor effluent is condensed and pumped to the etherification unit.

Octane improvement options

The reduction of sulfur in FCC gasoline by hydrodesulfurisation also results in some saturation of the olefins in the gasoline, regardless of the technology applied, and in undesired octane loss. However, the technologies discussed in the previous sections can be employed to minimise the adverse impact on the gasoline pool octane. This section discusses different technology options and their impact on important gasoline properties such as sulfur content, olefins content and octane rating.

Option 1: new versus traditional technologies

Octane loss in FCC gasoline hydrodesulfurisation depends on the feed sulfur content, feed olefin content, and the desired product sulfur content. The greater the feed sulfur content and the feed olefin content, and the lower the product sulfur content, the higher the octane loss.

As described earlier, the selective treatment of the different cuts of FCC gasoline makes the CDHydro/CDHDS process very effective in minimising the olefin loss and hence the octane loss of gasoline (Figure 7). Additionally, the olefin hydroisomerisation reactions taking place in the CDHydro process provide a mild octane boost. Unlike CDTECH technologies, traditional technologies do not treat the mid and heavy portions of gasoline selectively and thus incur higher octane loss.

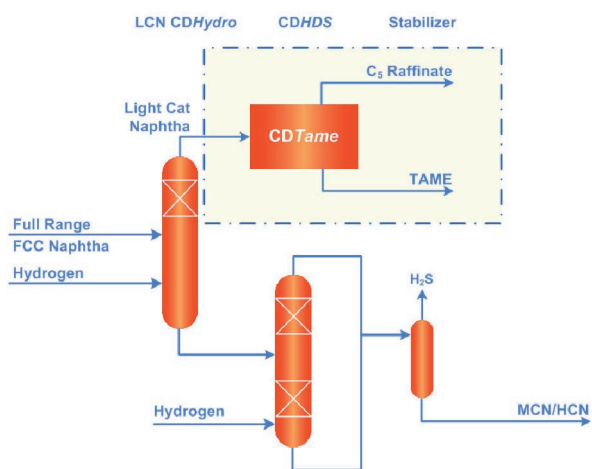


Figure 8. Addition of a TAME unit.

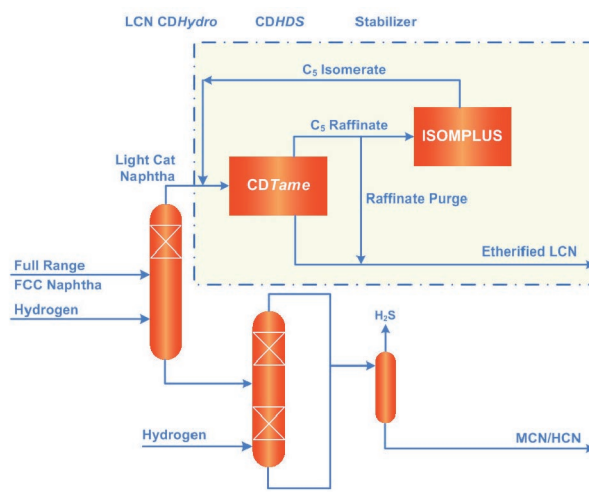


Figure 9. Addition of etherification and skeletal isomerisation.

For conventional processes, the typical octane loss is in the order of 0.5 - 2 (RON) octane points, relative to the full range naphtha stream. Due to the lower severity used in the CDHydro/CDHDS process, the octane loss tends to be 0.1 - 0.5 octane points lower (i.e. loss of 0.4 - 1.5 octane points).

Option 2: addition of etherification

A refiner operating an FCC unit has the opportunity to produce TAME from the isoamylenes contained in the LCN stream (Figure 8).

The LCN stream has high RVP and, due to the presence of olefins, is a high octane stream. If the gasoline pool is not constrained by RVP or olefins, this stream can be blended directly into the gasoline pool. However, a better option is to etherify the LCN to produce higher octane TAME product. If most of the isoamylenes in the LCN are converted to TAME, it can provide sufficient octane gain to compensate for the octane loss resulting from olefin saturation in the FCC gasoline desulfurisation unit.

By replacing the isoamylenes with TAME in the gasoline pool, the olefin content in the gasoline pool is reduced significantly. Since TAME has a low RVP, it depresses the RVP of the gasoline pool, which in turn provides the flexibility of blending more high RVP components such as C₅s, ethanol or isomerate.

Option 3: addition of etherification and skeletal isomerisation

The benefits of higher octane, lower RVP and lower olefin content offered by etherification can be further enhanced using ISOMPLUS skeletal isomerisation to convert the normal olefins to isoolefins (Figure 9).

With skeletal isomerisation, ether production can typically be boosted by another 50 - 80%. The corresponding octane gain from the combination of CDTame etherification and ISOMPLUS skeletal isomerisation technologies would be in the order of 1.5 points relative to the full range naphtha.

This octane gain compensates for the octane loss from processing highly olefinic FCC naphtha in an FCC gasoline desulfurisation unit, or it results in an overall octane gain for the combination of CDHydro/CDHDS and CDTame/ISOMPLUS technologies.

If olefins reduction is of interest, the combination of TAME production and C₅ skeletal isomerisation is advantageous because the majority of the C₅ olefins are converted to TAME, resulting in a dramatic reduction in olefin content.

Conclusion

The ever tightening fuel specifications are adding more constraints to refining operation and flexibility. These fuel specifications, specifically the reduction in sulfur and benzene content, are causing a reduction in gasoline octane value. With increasing demand for high octane gasoline, the refiner often has to invest in new refining processes such as FCC, reforming and isomerisation.

The production of TAME provides an effective option to offset the octane pool deficit and solve octane constraints in the refinery. Additional TAME production can be achieved by skeletal isomerisation of n-pentenes. If the production of biofuels is required in the future, the TAME unit can be easily retrofitted to produce TAEE by substituting methanol with ethanol. TAEE is easier to blend into the gasoline pool than ethanol. 