

# **Sulfur Reduction with Increased Octane and Yields**

## **CDTECH**

### **Introduction**

Today, many refiners are implementing projects to produce low sulfur gasoline, nominally at 30 to 50 ppm sulfur depending on local regulations and starting up the unit in the 2002 to 2005 timeframe. However, the savvy refiners also have another target in mind as they make key decisions on their current projects. These refiners recognize that the 10 ppm sulfur level being sought by auto makers will most likely happen in the 2005 to 2010 period. In order to avoid regret capital expenditures, they are taking a detailed look now, at what will be required to achieve 10 ppm, even though they may not make the final capital commitments until later.

CDTECH's approach to FCC gasoline desulfurization utilizes two catalytic distillation technologies. The first step is the CDHydro process, which separates the light catalytic naphtha (LCN) from the gasoline and treats it by removing mercaptan sulfur, selectively hydrogenating the dienes and converting alpha olefins to beta olefins. The treated LCN has very low sulfur content, higher octane and is suitable for etherification or alkylation. The remaining gasoline is selectively desulfurized in the CDHDS process. The resulting treated full range FCC gasoline has very low sulfur with minimal octane loss.

As the sulfur level in the treated product is reduced to lower and lower levels, the octane loss increases due to additional olefin saturation. However, options exist for regaining the octane loss and also increasing the yield of gasoline at the same time. This involves review and upgrading of the existing FCC unit technology and operation. Upgrading the FCC unit to include advanced technology features would result in significant increase in conversion, gasoline yield, and higher octane. This would boost refinery revenues. Therefore, when FCC revamp project is considered along with FCC gasoline HDS project, economics could justify both the projects. The following sections describe the CDTECH FCC gasoline HDS technologies and the ABB Lummus Global FCC technology features in detail. In addition, a case

study is presented to demonstrate the economic advantages of implementing these technologies as a single project.

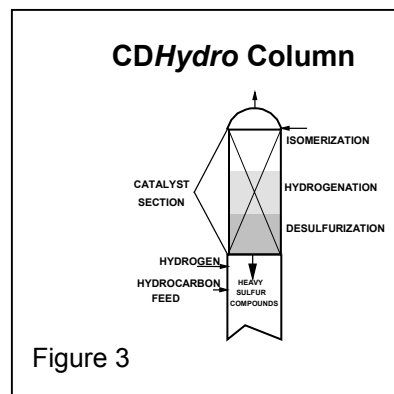
### **Desulfurization via Catalytic Distillation**

CDTECH has configured a process scheme that uses two stages of catalytic distillation (CD) to achieve greater than 99.5% desulfurization of FCC gasoline while maintaining high yield and minimal octane loss. The first stage is a *CDHydro*<sup>®</sup> dehexanizer, which processes typical FCC gasoline to produce an overhead C<sub>5</sub>/C<sub>6</sub> stream with very low diolefins and mercaptans. This stream does not require caustic treating for mercaptan removal. In fact, with greater than 99% removal of mercaptan sulfur, the *CDHydro* distillate product sulfur level is even lower than that achievable via caustic treating. The second stage uses the *CDHDS*<sup>®</sup> process to remove up to 99.5% of the sulfur from the heavier FCC gasoline while minimizing octane loss. For the refiner who wants to reduce gasoline from 300 ppm to 30 ppm, the recombined FCC gasoline sulfur can be reduced by 90% with virtually no yield loss and an octane loss of less than 1.0 (R+M)/2 for FCC gasoline streams containing about 30% olefins. Both steps are further described below:

### ***CDHydro* Light Gasoline Treating**

Conventional treating of LCN by extractive caustic systems is not sufficient for future gasoline sulfur levels. In addition, if the LCN is sent to an etherification or alkylation unit, removal of diolefins will be required for optimum operation of those processes. An application of CD that addresses all of the above problems has been developed and commercialized. The new application combines selective hydrogenation and distillation and is called the *CDHydro* process. It is applied by placing structured *CDModules*<sup>SM</sup> (distillation packing containing selective hydrogenation catalyst) in the top of a deisohexanizer and adding hydrogen below the catalyst (Figure 3). It operates at pressures significantly lower than conventional fixed bed reactors. As a result, hydrogen compression is normally not required.

In the bottom of the catalyst zone, mercaptans react with diolefins to form olefinic sulfides. These compounds have higher boiling points than the C<sub>5</sub> fraction and are easily fractionated to the bottom product. The olefinic sulfides are thermally stable, unlike disulfides from caustic sweetening, and therefore do not decompose in the reboiler to cause other problems. The overhead stream is desulfurized without the use of caustic and essentially all sulfur leaves the column with the bottom product. The LCN product typically contains less than 1 ppm mercaptans and can be blended directly into the gasoline pool.



Additional hydrotreating functions can optionally be achieved in the CDHydro column. In the upper section of the catalyst, hydrogen reacts with C<sub>5</sub> diolefins to selectively produce olefins. The overhead stream is low in diolefins, reducing gasoline gum formation and improving the quality of the LCN for etherification feedstock. Other benefits of selective hydrogenation are reduced RVP and increased octane of the C<sub>5</sub> cut. The double bond isomerization accompanying selective hydrogenation is responsible for both effects. Moving the double bond from the alpha to the beta position on the molecule converts 3-methyl butene-1 to 2-methyl butene-2 or 2-methyl butene-1, and converts pentene-1 to cis or trans pentene-2. In both cases, the beta position molecule has lower vapor pressure and higher octane than the alpha position molecule. This effect can increase the octane of the full range FCC gasoline by up to 0.5 (R+M)/2. The same types of reactions take place in heavier FCC gasoline components

Another benefit of catalytic distillation is long catalyst life. Conventional fixed bed hydrotreating catalyst gradually loses catalyst activity because the olefinic materials form oligomer intermediates that eventually turn to coke. The coke fouls the conventional fixed bed catalyst by blocking pores. Unlike conventional processes, the distillation environment removes the oligomer intermediate from the catalyst zone before it can form coke. This is because the intermediate has a much higher

boiling point than the reactants and can easily be separated by fractionation. As a result the catalyst zone stays very clean and maintains high catalyst activity for much longer times than conventional fixed bed catalysts. Currently, there are five *CDHydro* units in operation on FCC gasoline feedstock: All of these units are in operation with the original charge of catalyst. No regeneration has been performed and there has been no permanent loss of catalyst activity.

### **CDHDS Process**

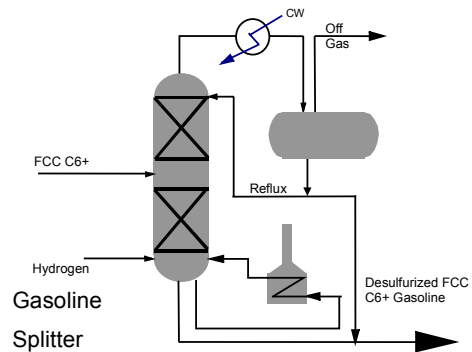
The *CDHDS* process is another recent development of catalytic distillation that combines hydrodesulfurization and distillation. Sulfur reduction of up to 99.5% has been demonstrated for FCC gasoline. A typical process scheme is presented in Figure 4.

The *CDHDS* column is equipped with *CDModules* containing HDS catalyst and is operated to produce most of the gasoline as

overhead product with heavy ends as bottom product. Hydrogen is added to the column bottom and sulfur-containing compounds are converted to H<sub>2</sub>S and hydrocarbons. Most *CDHDS* applications are designed to achieve about 90 to 99% hydrodesulfurization of the entire feed stream at substantially lower operating pressure than the 25 to 35 barg required by conventional processes.

Conducting the hydrodesulfurization reaction within a distillation tower offers the unique capability to achieve high sulfur conversion with minimal octane loss. This is accomplished by fractionating the light ends into a low temperature zone while the heavy ends are concentrated into a high temperature zone. As a result, the highly olefinic light ends are not exposed to the high temperatures that would cause considerable olefin saturation, but are still highly desulfurized at the relatively low temperatures in the upper section of the column. Meanwhile, in the bottom section

**CDHDS Process**



**Figure 4**

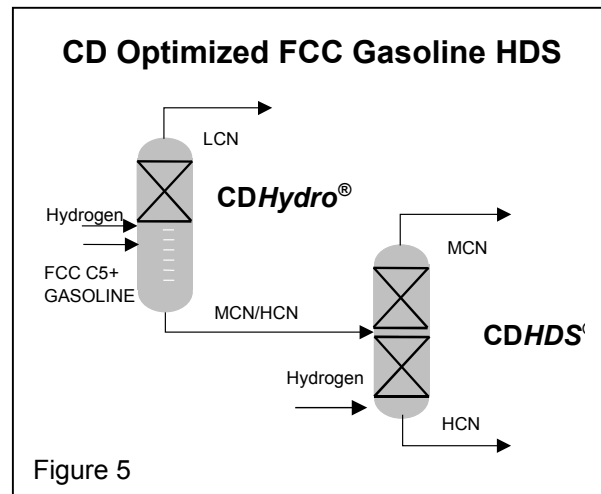
of the tower, the heavy ends are subjected to the higher temperature required to desulfurize the more refractory sulfur compounds in that fraction.

The separation of HDS zones available with *CDHDS* also helps to minimize the formation of recombinant mercaptans. In the bottom of the column, where the temperature is high enough for recombination to be kinetically active, there is virtually no H<sub>2</sub>S due to reboil vapor and hydrogen stripping, and there is already little olefin content in the heavy FCC gasoline fraction. Since the mercaptans always have a higher boiling point than the olefins that form them, the fractionation at the top of the tower tends to keep the mercaptans in the tower thus limiting the overhead product to low mercaptan level. Limited mercaptans are produced, but within normal product sulfur specifications. With lower sulfur targets, additional positive control measures are provided.

In conventional fixed bed reactors, most of the olefin saturation occurs in the lighter portion of the gasoline because the lower molecular weight olefins are easier to saturate. The lighter olefins also have higher octane than the heavy olefins, thus increasing the octane loss. The *CDHDS* process tends to saturate more of the heavy olefins and as a result has lower octane loss than conventional fixed beds at the same olefin saturation level. Alternately stated, at the same octane loss, the *CDHDS* process has greater olefin reduction. This is an additional benefit when the refiner needs to reduce olefins in gasoline.

As a result of operating at relatively low pressure, a make-up hydrogen compressor is not required. Also, with low olefin saturation, chemical hydrogen consumption is much lower than conventional HDS processes. Heat integration with the *CDHydro* column minimizes total energy consumption.

CDHDS also has long catalyst life is due to the *CDModules* and can exceed a five year FCC turn-around cycle, with no regeneration required. Conventional fixed beds will normally require at least one shutdown during the FCC cycle to regenerate or replace the catalyst. The capital cost of the conventional HDS units will be increased by the need for regeneration equipment, temporary storage tanks and additional feed pumps in the tank farm.



### Optimized FCC Gasoline HDS

The basic process flow scheme for desulfurization of Full Range Catalytic Naphtha (FRCN) is shown in Figure 5. The *CDHydro* process is used to produce sweet LCN with very low mercaptan content. The *CDHDS* process is used to desulfurize the MCN and HCN fractions. The combination of the two catalytic distillation processes provides refiners with cost effective reduction of sulfur in the gasoline pool at minimum capital cost and octane loss. There are currently three units in commercial operation with several more scheduled for start-up during 2002 to 2004.

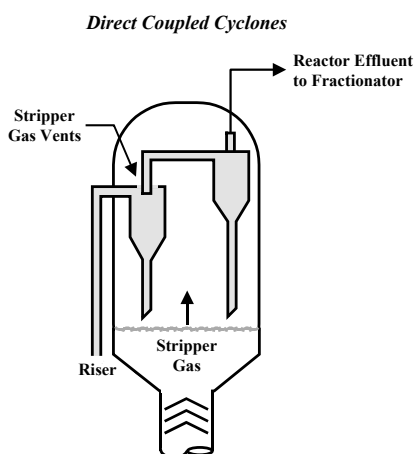
### III. Regaining the Octane Loss and Improving FCC Yields The Lummus

#### FCC Process

The octane loss due to gasoline desulfurization can be more than made up by implementing some minor modifications to the FCC unit. ABB Lummus Global licenses FCC technology which, or parts of which, can be applied to the existing unit to regain the octane loss and also improve yields of gasoline and other valuable products. The resulting improved profitability of the FCC unit could economically justify investment not only in the FCC technology upgrade but also in the gasoline desulfurization unit.

A few of the Lummus FCC technology features are described here which can produce the results as mentioned above. Also a case study is presented to substantiate the economic benefits of these technology upgrades.

The octane loss due to gasoline desulfurization can be compensated by operating the unit at a higher temperature. However, operation at higher temperature would produce more dry gas that could overload the wet gas compressor and also decrease selectivity of valuable products. To reduce dry gas production, the refiner needs to evaluate the reaction termination device (RTD). In some of the older units,



the RTD may not be the state-of-the-art due to which product vapors residence of time in the reactor vessel is high. That leads to post riser non-selective cracking reactions resulting in degradation of product slate. Lummus FCC process uses Direct Coupled Cyclones as the reaction termination device. This system is very effective in minimizing post riser residence time and recovering nearly 100% of the product at end of the riser. The delta coke goes down significantly which reduces regenerator temperature. All these effects lead to improved

yields and selectivity of valuable products. Salient features of this system are described below:

### **Direct Coupled Cyclones**

This state-of-the-art system consists of primary cyclones directly connected to the riser outlet and the secondary cyclones directly connected to the primary cyclones.

The Lummus Direct Coupled Cyclones system reduces post-riser residence time by an order of magnitude compared to conventional reaction systems, for example, 20 seconds down to 2 seconds. This minimizes the undesirable effects of post riser secondary cracking and hydrogen transfer reactions.

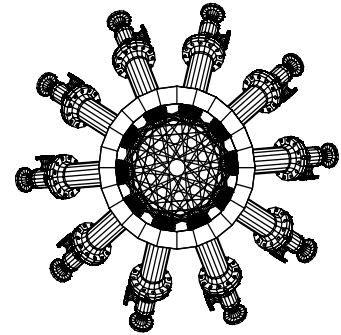
A unique feature of the Direct Coupled Cyclones is that the primary cyclone is at a pressure that is lower than that in the cyclone containment vessel. This cyclone pressure balance is similar to that which has been successfully used in FCC cyclones for over 50 years. The trickle valve at the bottom of the dipleg of the primary cyclone has a special feature that lets a small part of the stripper gas flow up the dipleg. This provides pre-stripping of the spent catalyst and ensures stable flow of catalyst down the dipleg as the gas and the catalyst flow counter-currently. This system results in negligible entrainment of hydrocarbon product vapors down the dipleg and into the stripper. In other words, recovery of hydrocarbon vapors at the end of the riser is almost complete.

### **Micro-Jet Feed Atomizer System**

Another technology that refiner need to evaluate or consider is the feed injectors. Thorough catalyst/oil contact and quick vaporization of feed is very important in maximizing conversion, and hence, yields of valuable products. Lummus offers state-of-the-art radial feed injection system that has shown significant yield improvements in many commercial applications.

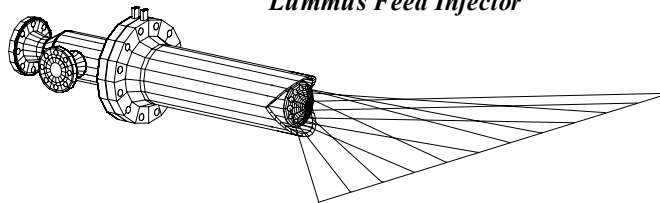
The **Micro-Jet** feed atomizer system is designed to efficiently atomize and distribute the oil feed uniformly across the riser. Thorough contact of the oil with hot regenerated catalyst promotes rapid vaporization and quick initiation of the cracking reactions. This results in higher conversion for a given riser volume and temperature. Thus, riser efficiency is improved with increased conversion at the same in riser outlet temperature. The proprietary atomization technique uses steam to atomize the feed and minimize oil side pressure drop.

*Radial Feed Injection*



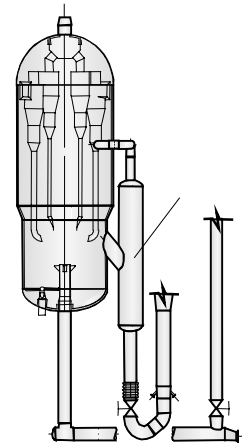
Each atomizer is equipped with a specially designed tip which generates several smaller sprays or *Micro-Jets*. Each individual jet is arranged to collectively form a flat fan spray pattern with all the jets combined. This design ensures uniform distribution of feed across the riser at an optimum velocity that avoids erosion and catalyst attrition.

*Lummus Feed Injector*



### **Catalyst Circulation**

Some units may be limited by catalyst circulation, or the catalyst circulation is not stable, due to which the yields are compromised. In such situations, the refiner should consider modifying the system to improve unit performance. Lummus offers a catalyst circulation system that requires lower regenerator elevation and air blower pressure for a given catalyst circulation rate and provides stable and uniform catalyst flow to the riser.



The catalyst is withdrawn from the regenerator in an external withdrawal hopper where the bigger air bubbles that might be entrained with the catalyst are removed. The catalyst density in this hopper is adjusted so that it is significantly higher than the regenerator bed density. The catalyst enters the regenerated catalyst standpipe at the optimum density and flow conditions that provide maximum static head build up. The regenerator standpipe entry is a proprietary Lummus design feature that ensures smooth standpipe operation. The regenerated catalyst standpipe (RCSP) is all vertical. The regenerated catalyst flows to the riser through a J or Y-bend that is designed so that lateral distance over which the catalyst has to move is minimized.

The spent catalyst flows down the stripper into a vertical standpipe and then is lifted back into the regenerator through a unique square-bend transfer line that discharges the catalyst into the center of the regenerator where it gets uniformly distributed. This system of spent catalyst transfer is not only stable but helps to achieve uniform catalyst regeneration due to discharge of the spent catalyst in center of the regenerator.

#### **IV. Case Study:**

The case study presented below considers revamping an existing unit to install the Lummus Micro Jet feed injection system and Direct Coupled Cyclones. The pre and post revamp yields, product properties, and operating conditions are summarized in Table 2. The post revamp yields and product properties are after gasoline desulfurization using CDTECH technology to reduce sulfur from 1330 ppm to 75 ppm for a 50 ppm gasoline pool. The FCC unit chosen for this case study operates with feed rate of 6489 tonnes/day.

The total cost of the FCC revamp is estimated to be US\$ 7 MM. Cost of the CDTECH gasoline desulfurization unit is estimated to be US\$ 23 MM. The product prices used for the economic analysis are summarized in Table 2.

Based on the above, the incremental revenue is estimated to be \$12 MM per year including the HDS operating costs. The simple payout of the whole project i.e. FCC revamp along with gasoline desulfurization is calculated to be about 2.5 years. This would meet typical economic justification required by the industry for pursuing a project. Operating the HDS unit to a product sulfur level of 15 ppm will reduce the product octane increase and result in a somewhat longer payout time.

It may be noted that the cost of FCC unit revamp is only 20 % of the total cost of the project. Yet, it can provide economic incentive for carrying out the environmentally mandated FCC gasoline desulfurization project.

**Table 1  
Economic Analysis**

	Yields				Product Prices \$/ ton	Delta Yields tons / day	Delta Revenue \$/ day
	Pre Revamp		Post Revamp Feed Injectors + RTD + HDS				
Component	wt%	vol%	wt%	vol%			
Product Yields							
Perfect Fractionation Basis							
H2S	0.1	---	0.1	---			
H2	0.07	---	0.08	---			
C1	0.67	---	0.78	---			
C2	0.63	---	0.66	---			
C2=	0.65	---	0.84	---			
Total H2-C2=	2.02	---	2.36	---	140	22.1	3,089
C3	2.02	3.53	2.22	3.88			
C3=	4.93	8.38	6.64	11.29			
iC4	4.32	6.79	3.93	6.17			
nC4	2.18	3.3	2.19	3.31			
C4=	7.72	11.27	9.63	14.04			
Total C3-C4 LPG	21.17	33.27	24.61	38.69	249	223.2	55,582
DB Naphtha C5 – 221 oC	50.6	61.72	53.24	64.75	245 + 6.5	171.3	62,832
LCO (221 – 354 oC)	11.72	11.34	7.85	7.45	170	-251.1	-42,691
HCO (354 C+)	9.56	8.44	6.54	5.66	140	-196	-27,435
Coke	4.83	---	5.30	---			
Total	100	114.77	100	116.55			
Conversion @ 221 oC	78.72	80.22	85.61	86.89			
Gasoline Octanes, RON/MON	90.9 / 79.6		91.4 / 80.0				
Gasoline Sulfur, wppm	1330		75				
Operating Conditions							
Riser Outlet Temp., oC	518		544				
Regenerator Temp., oC	705		715				
Feed Rate, tons / day	6,489		6,489		170		
Total							51,377