

# CDTECH Selective FCC Gasoline Sulfur Reduction

*CDHydro*® , *CDHDS*® , *CDHDS+*®



Lummus Technology  
a CB&I company

## Overview

Full range catalytic naphtha (FRCN) is a major component of gasoline and is also the single largest contributor of sulfur to the gasoline pool. In order to meet increasingly strict government regulations, it is essential that refiners implement measures to reduce sulfur in FRCN.

CDTECH® (Catalytic Distillation Technologies) offers several commercially proven process technologies that selectively reduce sulfur in FRCN. The CDHydro®, CDHDS® and CDHDS+® processes use the principle of catalytic distillation to reduce sulfur to as low as 10 ppm while retaining most of the octane value in FRCN without yield loss, allowing refiners to meet even the most severe gasoline sulfur regulations. Furthermore, since olefin saturation is minimal, hydrogen consumption is low, resulting in low operating costs.

## Key Process Advantages

### High conversion and low octane loss

Commercial units using CDHydro, CDHDS and CDHDS+ processes have reduced the FRCN sulfur level by more than 99 percent. Total sulfur levels in the gasoline pool of 10 ppm and less are readily achievable and have been demonstrated. This is accomplished with less octane loss than other selective hydrodesulfurization (HDS) processes because with catalytic distillation, the desulfurization severity applied to the different fractions of the FRCN match the severity required for the particular sulfur species present in the respective fraction. This approach, in combination with the inherent reaction dynamics in a catalytic distillation column, suppresses olefin saturation. The actual octane loss will depend on the overall sulfur target in the gasoline pool and volume of other blending components; however, an FRCN (R+M)/2 octane loss of less than 1.5 numbers is typical for a 10 ppm sulfur pool.

### Long catalyst life

Catalyst life in commercial CDHydro, CDHDS and CDHDS+ process units exceeds FCC run-length. This ensures that catalyst replacement will only be required at scheduled FCC turnaround intervals, eliminating the need for catalyst regeneration equipment and temporary gasoline storage and pumping facilities.

Conventional fixed-bed processes tend to lose significant catalyst activity

over the run-length due to fouling of the catalyst, and normally require selective hydrogenation to remove diolefins prior to the HDS reactor. Even then, these processes cannot meet the FCC run-length without a shutdown to regenerate catalyst.

A catalytic distillation column minimizes catalyst fouling – and hence deactivation – by continuously washing the catalyst with internal reflux and removing heavy precursors before they foul the catalyst. As a result, both the CDHydro and CDHDS processes maintain high catalyst activity and high selectivity throughout the



ChevronTexaco CDHydro/CDHDS unit at Pembroke, UK

FCC run-length. This means lower average octane loss over the full cycle compared to fixed-bed HDS processes.

### Flexibility to process feedstocks with a wide range of sulfur concentration

A refinery's economics depends on processing crudes from a variety of sources, which inevitably means a range of sulfur levels in the feedstock to the gasoline desulfurization unit. CDTECH's catalytic distillation units are able to process feedstocks with high sulfur content and still achieve high sulfur conversion with low octane loss. The processing flexibility of the CDHydro and the CDHDS columns is a result of the ability to vary the desulfurization severity applied to different cuts of the gasoline by using handles such as operating pressure and cut points.

### Catalytic distillation environment

The unique advantages of the catalytic distillation environment are:

- Greater safety and stability (no danger of hot spots or runaway reactions as a

Performance
<ul style="list-style-type: none"><li>Octane loss less than 1.5 (R+M)/2 for 10 ppm sulfur pool</li><li>Demonstrated on full range naphtha<ul style="list-style-type: none"><li>Not limited to gasoline with low olefins or low endpoint</li></ul></li><li>Less than 10 ppm sulfur product<ul style="list-style-type: none"><li>Achieve 99+% desulfurization</li></ul></li><li>CDTECH's commercial units on real feedstocks have met guarantees<ul style="list-style-type: none"><li>Easier to operate than fixed bed reactors</li><li>No caustic treatment required for mercaptan control</li></ul></li></ul>
Flexibility
<ul style="list-style-type: none"><li>Handles feedstock swings</li><li>T<sub>90</sub> control with no additional investment</li><li>Investment can be staged as sulfur specifications get tighter</li></ul>
Reliability
<ul style="list-style-type: none"><li>Guaranteed 5+ years catalyst life meets FCC cycle without:<ul style="list-style-type: none"><li>Shutdowns for catalyst replacement</li><li>Spare equipment</li><li>Additional tankage</li><li>Selective hydrotreating</li><li>Extra run-off capacity</li></ul></li><li>No catalyst disposal issues</li></ul>

result of sudden changes in feedstock composition)

- Long catalyst life because the catalyst is continuously washed by the liquid traffic in the column
- Higher reliability since the catalyst is less susceptible to deactivation by fouling (wash effect) and to poisoning (counter-current effect)
- The multi-phase environment allows a lower operating pressure (low hydrogen partial pressure), the use of low purity hydrogen, and operation without the large hydrogen recycles needed by fixed-bed processes to reduce fouling and to minimize mercaptan formation.

The presence of olefins in the process



Irving Oil CDHydro/CDHDS unit located at St. John, New Brunswick, Canada

combined with the  $H_2S$  produced during desulfurization can lead to recombination, forming heavy mercaptans. Catalytic distillation minimizes mercaptan formation by using distillation to position them in the catalyst zone where they decompose.

### Process Description

Selective FRCN sulfur reduction begins with fractionation of the light naphtha overhead in a CDHydro column. Mercaptan sulfur reacts with diolefins to produce heavier sulfur compounds, and the remaining diolefins are partially saturated to olefins by reaction with hydrogen. Bottoms from the CDHydro column, containing the reacted mercaptans, are fed to the CDHDS column where mid and heavy cat naphtha are catalytically desulfurized in

two separate reaction zones. HDS conditions are optimized for each fraction to achieve the desired sulfur reduction with minimal olefin saturation. The three desulfurized fractions can be made available as separate product streams for further processing or blending.

These process technologies have been fully commercialized on challenging feeds having both high olefin and high sulfur content. Long term operation has demonstrated robust characteristics and long catalyst life, exceeding ten years continuous operation in CDHydro process units and five years in CDHDS process units.

Optionally, a second stage of desulfurization improves performance with even higher octane retention while achieving very low sulfur content. This version, the CDHDS+ process, also maintains high HDS performance during refinery upsets.

No cracking reactions occur in the process, so yield losses are essentially eliminated with vent gas recovery. The product streams are stabilized as appropriate for the individual refinery. The two columns are heat integrated to minimize energy requirements and the configuration is customized for site-specific availability of utilities and energy conservation objectives.

Hydrogen is typically utilized on a once-through basis in the CDHydro column. It is usually supplied to the CDHDS column at typical reformer hydrogen pressure levels, without additional compression. Optimal integration with hydrogen generation and sour gas treating facilities at most sites will include hydrogen recycle and CDHDS vent gas treating within the process.

In the CDHDS process, the recombina-

tion of olefins and hydrogen sulfide to form mercaptans is limited. Since there is no need to over-saturate olefins in order to achieve ultra-low sulfur levels, octane loss is minimal.

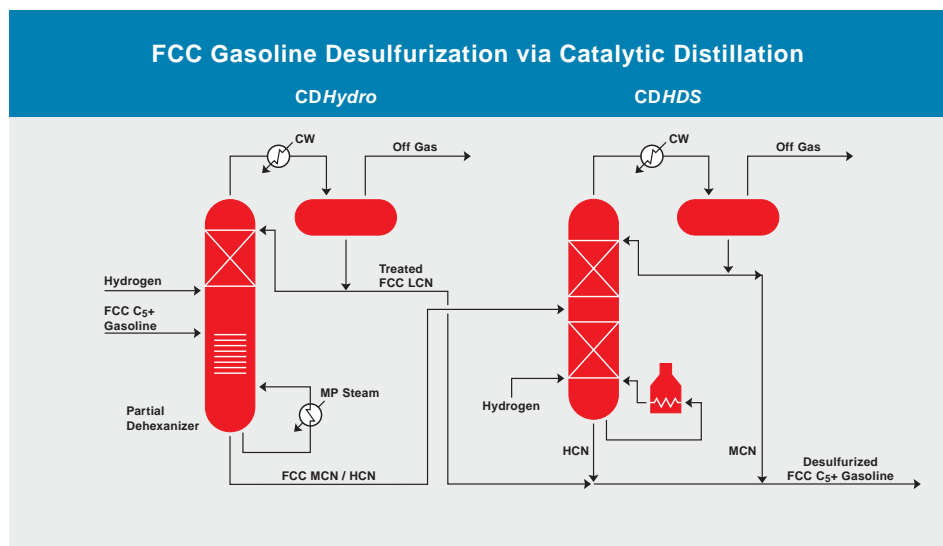
### Commercial Experience

Over one million barrels per standard day (BPSD) of gasoline is treated using the CDHydro, CDHDS and CDHDS+ processes. These technologies have been selected by leading refining companies – Chevron, Shell, Motiva, Valero, Agip ENI, Irving Oil, Hellenic, and PetroChina – for multiple site applications. The CDTECH process technologies are working in large units and small units, with high feed sulfur and low feed sulfur, all meeting or besting the target product sulfur level and with low octane loss.

### Summary

The combination of the CDHydro, CDHDS and CDHDS+ processes gives refiners low capital and operating cost solutions for gasoline sulfur reduction. In addition, low hydrogen consumption, high octane retention, and long catalyst life minimize changes required in other refinery processes.

These processes are members of a family of technologies developed and commercialized by CDTECH for use in the petroleum refining and petrochemical industries. CDTECH is a partnership between Lummus Technology, a CB&I company, and Chemical Research and Licensing, a CRI company.



## Process Technologies from CDTECH

CDHydro <sup>®</sup>	Selective hydrogenation using catalytic distillation: <ul style="list-style-type: none"> <li>▫ MAPD reduction in mixed C<sub>3</sub>S</li> <li>▫ C<sub>4</sub> diolefins reduction in mixed C<sub>4</sub>S (hydroisomerization option)</li> <li>▫ C<sub>4</sub> acetylenes reduction in mixed C<sub>4</sub>S</li> <li>▫ C<sub>5</sub> diolefins reduction in mixed C<sub>5</sub>S (hydroisomerization option)</li> <li>▫ C<sub>6</sub> diolefins reduction in mixed C<sub>6</sub>S (hydroisomerization option)</li> <li>▫ Benzene reduction in LSR and reformat streams</li> <li>▫ Mercaptan reduction in C<sub>4</sub>/C<sub>5</sub>/C<sub>6</sub> olefinic streams</li> <li>▫ Hydrogenation of DIB to IsoOctane</li> <li>▫ Hydrogenation of benzene to high purity cyclohexane</li> </ul>
CDHDS <sup>®</sup> and CDHDS+ <sup>®</sup>	Desulfurization using catalytic distillation: <ul style="list-style-type: none"> <li>▫ FCC gasoline</li> <li>▫ Jet fuel/kerosene</li> </ul>
ISOMPLUS <sup>®</sup>	Isomerization of n-olefins to iso-olefins
Dimer <sub>s</sub> <sup>®</sup>	Dimerization of iso-olefins in C <sub>4</sub> streams*
CDAlky <sup>®</sup>	Alkylation of C <sub>4</sub> olefins with isobutane
CDCumene <sup>®</sup>	Alkylation of benzene with propylene
CDIB <sup>®</sup>	Decomposition of MTBE to high-purity isobutylene
CDAcrylamide <sup>®</sup>	Hydration of acrylonitrile to acrylamide
CDTECH EB <sup>®</sup>	Alkylation of benzene with ethylene
BASF SELOP	Selective hydrogenation of C <sub>4</sub> S and C <sub>5</sub> S for diolefin reduction
Sulzer Butene-1	Superfractionation of mixed C <sub>4</sub> S to produce high-purity butene-1
CDMtbe <sup>®</sup>	MTBE production from mixed C <sub>4</sub> S and methanol
CDEtbe <sup>®</sup>	ETBE production from mixed C <sub>4</sub> S and ethanol
CDTame <sup>®</sup>	TAME production from mixed C <sub>5</sub> S and methanol
CDTae <sup>®</sup>	TAEE production from mixed C <sub>5</sub> S and ethanol
CDEthers <sup>®</sup> methanol	Coproduction of MTBE and TAME from mixed C <sub>4</sub> /C <sub>5</sub> S and methanol
CDEtherol <sup>®</sup>	Selective hydrogenation of diolefins combined within ether processes above

\* offered jointly with Snamprogetti



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