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FCC naphtha post-treatment

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Agenda

• Why post-treatment of FCC naphtha?
• The new sulfur challenge
• Molecular understanding of FCC naphtha
• Post-treatment step-by-step
• Octane loss prediction model
• Haldor Topsoe’s HyOctane Technology (HOT™)
Why post-treatment of FCC naphtha?
Typical gasoline pool composition

Percentage of blend stocks of pool volume

- FCC naphtha: 36%
- Reformate: 34%
- Alkylate: 12%
- Hydrocracked naphtha: 12%
- Coke naphtha: 2%
- Isomerate: 5%
- Light SR naphtha: 3%
- Butanes: 5%
- MTBE: 2%
Typical gasoline pool composition

Distribution of sulfur in blend stocks

- Light SR naphtha: 1%
- Coker naphtha: 1%
- FCC naphtha: 98%
FCC feed sulfur vs. gasoline sulfur

FCC pretreat
- FCC pretreat feed S~1-3 wt %
- FCC feed S~200-2000 wt ppm

FCC
- FCC product naphtha sulfur, wt ppm

FCC gasoline
- FCC gasoline S~10-100 wt ppm

Graph showing the relationship between FCC feed sulfur and gasoline sulfur.
Why post-treatment?
Gasoline sulfur limits 2016

Legend:
- 0-10 ppm
- 11-30 ppm
- 31-50 ppm
- 51-150 ppm
- 151-500 ppm
- 501-2500 ppm
- No information

Countries may apply lower limits for different grades, regions/cities, or based on average content. Detailed information on limits and regulations can be found at www.stratasadvisors.com.

Source: Stratas Advisors, May 2016
Why post treatment?
Gasoline sulfur limits 2020
Octane loss
General trend

Octane loss increase with increasing sulfur removal
The value of octane

- Octane value increased 50% from 2010 to 2015.
- Octane value expected to continue due to lower sulfur limits.
- Octane retention during is increasingly important.
Molecular level understanding of FCC naphtha
Distribution of sulfur

Cumulative sulfur (%) vs. Temperature (°C)

- Mercaptans
- Thiophene
- C1-Thiophene
- C2-Thiophene
- C3-Thiophene
- Benzo-Thiophene

Light CN vs. Heavy CN

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Distribution of olefins

Light fraction
- High olefin concentration
- Low sulfur concentration
- Mercaptan sulfur

Heavy fraction
- Low olefin concentration
- High sulfur concentration
- Thiophenic sulfur

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Post-treatment step-by-step
Main function of the selective hydrogenation unit

- Selectively hydrogenation of di-olefins
  - Prevent fouling in downstream HDS reactors
- Transform light sulfur in to heavy sulfur
  - Low sulfur light fraction out of splitter
FCC naphtha
Sulfur speciation – SHU feedstock

- Gas chromatogram
- Sulfur specific detector (GC-AED)
Pilot plant test, Haldor Topsoe catalyst TK-703 HyOctane™ Selective Hydrogenation Unit (SHU), sulfur speciation – feedstock

Mercaptans
Pilot plant test, Haldor Topsoe catalyst TK-703 HyOctane™
Selective Hydrogenation Unit (SHU), sulfur speciation – product

- Heavy sulfides
- Light mercaptans
- Sulfur transformation
- Heavy sulfides
Pilot plant test, Haldor Topsoe catalyst TK-703 HyOctane™
Selective Hydrogenation Unit (SHU), sulfur speciation – product
Heavy naphtha desulfurization
Hydrodesulfurization of HCN

Layout

Topsoe’s TK-710 HyOctane™ and TK-747 HyOctane™ catalysts are well proven in the HDS reactor and the Mercaptan control reactor.
Octane loss prediction model
Octane loss prediction model

Foundation
- Based on molecular understanding.
- Large database with detailed chemical analysis (759 components) of commercial and pilot plant feed and product samples.
- Intelligent reduction of complexity by the discovery of a manageable number of key reaction paths that govern octane loss.

Model flexibility
- Unit design (splitter, number of HDS reactors).
- Final boiling point of feed.
- Feed and Product sulfur
Key reaction path example
Making 2-methylpentane

Reactants, average RON = 100

\[
\begin{align*}
\text{2-methylpentene-1} & \quad \text{H}_2\text{C} = \text{C} & \quad \text{H}_2\text{C} = \text{C} & \quad \text{H}_2\text{C} = \text{C} \\
& \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{2-methylpentene-2} & \quad \text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
& \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{4-methylpentene-2 (cis and trans)} & \quad \text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
& \quad \text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{2-methyl-1,4-pentadiene} & \quad \text{H}_2\text{C} = \text{C} & \quad \text{H}_2\text{C} = \text{C} \\
& \quad \text{CH}_2 \quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{Product, RON = 76} \\
\text{2-methylpentane}
\end{align*}
\]

\[\Delta \text{RON} = -24\]

Abundant + high impact reaction path
Model usage

Precise octane loss calculation regardless of feed, unit design and sulfur conversion
The Topsoe HyOctane Technology HOT™ Process
The Topsoe **HyOctane Technology HOT™ Process**

The new technology leap

- Deep catalyst understanding
- Deep kinetics and equilibrium understanding
- Extensive pilot work
- Use of process model for octane prediction
- Hydrotreating engineering capabilities
- Invention resulting in unmatched octane retention
Where does it apply?

New Refinery Configuration

Grassroots

Revamp

- Tighten sulfur spec
- More olefinic feed
- Higher sulfur feed
- Higher end point feed

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Changing operation from 30 to 10 wppm S gasoline in the traditional technology

Much higher RON loss with your existing process technology

Consequence

- Cut feed rate
- Cut end point of feed

And/or

Feed Naphtha curve

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The clear Octane advantage with the Topsoe HOT™ Process
The Octane vs HDS relation

- **Traditional technology**
  - At a product S of 10 ppm

- **Haldor Topsoe’s HOT™ Process**
Conclusion

• Topsoe’ HOT™ process reduces the octane loss for same product sulfur by 50-65%

• No need for reducing endpoint resulting in higher gasoline production

• Possible to process more higher sulphur crudes

• Possible to reduce the operating severity of the FCC pretreat unit

• Possible to cut deeper into the LCO to make more gasoline gasoline

Unmatched octane retention in your gasoline pool
Summary

• Sulfur reduction in the gasoline is being regulated to 10 wtppm in many parts of the world

• Sulfur reduction result in additional octane loss

• Haldor Topsoe’s model is capable of calculating the octane loss accurately by looking at the octane loss for each molecule and its reaction pathway

• Our HyOctane™ catalyst portfolio is well proven in today’s gasoline post treatment units

• Haldor Topsoe’s new and innovative HyOctane Technology (HOT™) for grassroots units and revamps will reduce the octane loss by 50-65% at the same product sulfur.