Reducing octane loss - solutions for FCC gasoline post-treatment services

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Agenda

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

Percentage of blend stocks of pool volume

- FCC naphtha: 36%
- Reformate: 34%
- Isomerate: 5%
- Hydrocracked naphtha: 2%
- MTBE: 2%
- Butanes: 5%
- Light SR gasoline: 3%
- Coker naphtha: 1%

Distribution of sulfur in blend stocks

- FCC naphtha: 98%
- Light SR naphtha: 1%
- Coker naphtha: 1%
Why post-treatment?

Gasoline sulfur limits 2016

Gasoline sulfur limits 2020
Octane loss

General trend

Octane loss increase with increasing sulfur removal

Octane loss

HDS conversion (%)
Molecular level understanding of FCC naphtha
Distribution of sulfur

Cumulative sulfur (%)

Temperature (°C)

Light CN

Heavy CN

Mercaptans

C1-Thiophene

C2-Thiophene

C3-Thiophene

Benzo-Thiophene

Light CN

Heavy CN
Distribution of olefins

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

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

![Graph showing distribution of olefins with carbon numbers C4 to C11 and total olefins (wt %) on the y-axis.](image)
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 into 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
Pilot plant test, Haldor Topsoe catalyst TK-703 HyOctane™
Selective Hydrogenation Unit (SHU), sulfur speciation – product

Light fraction

Heavy fraction

Sulfur free

Sample 2016209514
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

\[ \text{2-methylpentene-1} \xrightarrow{\text{2-methyl-1,4-pentadiene}} \text{2-methylpentene-2} \]

\[ \text{H}_3\text{C} = \text{CH}_2 \xrightarrow{\text{H}_2\text{C} = \text{CH}_2} \text{2-methylpentene-2} \]

\[ \text{H}_3\text{C} - \text{C} = \text{CH}_3 \xrightarrow{\text{cis and trans}} \text{4-methylpentene-2} \]

\[ \text{H}_3\text{C} - \text{C} = \text{CH}_3 \xrightarrow{\text{cis and trans}} \text{4-methylpentene-1} \]

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

Product, RON = 76

\[ \text{H}_3\text{C} - \text{C} = \text{CH}_2 \xrightarrow{\text{cis and trans}} \text{2-methylpentane} \]

Abundant + high impact reaction path

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Model usage

Precise octane loss calculation regardless of feed, unit design, and sulfur conversion

Input

Product space
Unit design

Process
conditions

Output

10 ml sample

Calculated
octane loss
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

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

Revamp
Changing operation from 30 to 10 wtppm S gasoline
Traditional technology

• Much higher RON loss with your existing process technology

Consequence

Cut feed rate
And/or
Cut end point of feed

Feed Naphtha curve
The clear octane advantage with the Topsoe HOT™ process
The octane vs HDS relation

The octane vs HDS relation

Traditional technology
At a product S of 10 ppm
Topsoe HOT™ process
Conclusion

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

• No need for reducing end point resulting in higher gasoline production

• Possible to process more higher sulfur crudes

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

• Possible to cut deeper into the LCO to make more 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 grassroot units and revamps will reduce the octane loss by 50–65% at the same product sulfur