FCC Gasoline Treating Using Catalytic Distillation

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Gasoline of the Future

- Lead is out
- Olefins reduced
- Aromatics reduced
- Benzene reduced
- Sulfur reduced
Gasoline Desulfurization Requirements

- Pool sulfur specification
  - Europe
    - European Union
    - 50 ppm max - 2005
    - 10 ppm max
    - - available 2005
    - - standard 2008
  - US, Canada
    - 30 ppm avg - 2002 to 2008
  - Future
    - 15 -10 -5 ppm? - 2005+
Sulfur Sources

- **FCC Naphtha**
  - 200 to 3000 ppm
  - 25 to 40% of refinery pool volume
  - 85 to 99% of refinery pool sulfur
Optimized HDS Process

- FCC C5+ GASOLINE
- LCN
  - Mild HDS
  - MCN/HCN
- MCN
  - Medium HDS
  - HCN
  - Severe HDS
Conventional LCN Treating

- Fractionate LCN from FCC Gasoline
- Caustic wash for mercaptan removal
  - ~90% effective
- Selective hydrogenation of dienes for alky/ethers
- Compression of makeup hydrogen

Diagram:
- LCN from FCC C5+ Gasoline
- Mercaptan Removal
- Selective Hydrogenation
- Hydrogen Compression
- Fresh Caustic
- Spent Caustic
- MCN/HCN
- FCC Gasoline

Hydrogen

Treated LCN
Hydrogenation / Distillation

- Replace trays with structured distillation packing containing catalyst
- Add Hydrogen Feed
- Vent excess Hydrogen
**CDHydro Reactions**

**Thioetherification**

\[
\begin{align*}
\text{C} & \equiv \text{C} - \text{C} - \text{C} + \text{C} & \equiv \text{C} - \text{C} - \text{SH} & \rightarrow \text{C} - \text{C} - \text{S} - \text{C} - \text{C} \\
\text{C} & \equiv \text{C} & \equiv \text{C} & + & \text{H} & \equiv \text{H} & \rightarrow & \text{C} & \equiv \text{C} - \text{C} - \text{C} - \text{C} - \text{C}
\end{align*}
\]
CDHydro Reactions

Isomerization

\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\]

RON

118
Hydroisomerization boosts full range FCC naphtha by 0.5 RON
Catalytic Distillation

Catalyst Section

Wire Mesh

H2

Reflux

Vapor

Catalyst

Catalyst Section Drawing
Optimized FCC Naphtha HDS

CDHydro®

Hydrogen
FCC C5+
GASOLINE

LCN

MCN/HCN

HDS
Conventional MCN/HCN HDS

Make-up Hydrogen

Reactors

Recycle Hydrogen

Light Ends

Stripper

CW

Light Ends

LP Steam

Low Sulfur FCC Gasoline

FCC Gasoline
Conventional Reactor Design

- Severity of reactor conditions set by most refractory species
  - Temperature
  - H₂ partial pressure
- Lighter sulfur species react to very high conversions
- All olefins exposed to the most severe conditions
Recombinant Mercaptan Experience

Mercaptan Levels

- RSH Level, ppm
- Octane Loss (R+M)/2
- fixed bed RSH

Graph showing the relationship between RSH Level (ppm) and Octane Loss (R+M)/2.
Optimized FCC Gasoline HDS

- FCC C5+ GASOLINE
- LCN
- Mild HDS
- MCN
- Medium HDS
- MCN/HCN
- Severe HDS
- HCN
MCN/HCN with CDHDS

Conditions milder than conventional fixed bed (17 barg vs 28+)

> 99% HDS
Heavy sulfur to bottom

Light olefins to top
Min octane loss(<1@ 90% HDS)

Low H2 consumption
Low sulfur bottoms product good for gasoline

No yield loss due to cracking
No makeup compressor
No mid-cycle shutdown for catalyst regen
No feed storage required
Olefin saturation is higher for heavy olefins
Octane vs. Carbon Number

RON Linear Olefin - Linear Saturate
Why is CDTECH’s octane loss lower?

- Conventional fixed bed hydrotreaters
  - Saturate primarily light olefins
  - Light olefin saturation causes high octane loss
- CDHDS
  - Higher saturation of heavy olefins
  - Less octane to lose in heavy olefins
  - Lower octane loss at a given olefin reduction
Fixed Bed HDS Catalyst Life?

- **FCC turnaround cycle**
  - Modern refineries target 5 year cycle
- **Conventional fixed bed hydrotreaters**
  - Olefins form oligomers
  - Oligomers form coke that fouls catalyst
  - Catalyst activity reduced
  - Regenerate or replace catalyst
  - Must shutdown before end of FCC cycle
  - Fixed bed catalyst life insufficient
Commercial Catalyst Activity for FCC Gasoline HDS

Relative Activity vs Days on Oil

- Fixed Bed HDS
Catalyst Activity History for Commercial CDHDS Units

Days Since Start-up

Observed Rate Const.

Irving Oil • Motiva • ChevronTexaco
Conventional Unit Restart

FCC unit \rightarrow Sulfur Reduction Unit

Untreated FCC Gasoline storage

Extra Capacity Required
Conclusions

**CDHydro**
- Lowest sulfur and diolefins in LCN
- Eliminates separate mercaptan and diolefin removal units

**CDHDS**
- Lowest FCC cycle olefin loss via HDS
- No cracking yield loss
- No diene pretreatment required
- No regeneration/feed storage required

**CDHydro/CDHDS**
- Lowest overall octane loss
- Commercially proven
- Most cost effective HDS in FR FCC CN
- Long catalyst life via catalytic distillation
- Low capital cost
Recommendations

• Plan for 10 ppm sulfur
• Evaluate full FCC cycle performance
• Include shutdown related capital cost
• Thank you to DOE for 1980 funding for CR&L