Utilizing the Flexibility of FCC Additives for Shale Oil Processing

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Shale Oil: The Game Changer

Rapid growth in shale oil production has been a game changer for the energy sector.

What’s the future for refinery shale oil processing?

The recent decline in crude price may curb shale oil production, but **shale oil will continue to be a significant portion of U.S. refinery crude input**.
Shale Oil Impact on FCC Operation

- More paraffinic FCC feed
  - Increased LPG production but lower olefinicity
  - Decreased gasoline octane
  - Lower delta coke
    - Often offset with increased residue processing

- Shift in FCC feed contaminants

- Lower cost butane resulting in increased Alky margins

How to optimize given the changing FCC operation?
FCC Additives Provide Flexibility

Use the Additive Approach

• Quick solutions to individual problems

• “On/Off” approach - can be used only when required

• Acts over and above the base catalyst thereby minimizing risk

• Can be used with any unit configuration & base catalyst formulation

• Provides a cost effective and timely solution to many problems
FCC Additives for Shale Oil Processing

- **CAT-AID™**
  - Iron and Vanadium trap
  - Increases conversion
  - Reduces fresh and/or flushing ecat addition rate
  - Improves catalyst fluidization properties

- **ZSM-5**
  - Increases LPG olefin production
  - Boosts gasoline octane

- Additive loaders and logistical solutions
  - Optimize additive addition and handling
Mechanism of Iron Poisoning

Ecat surface contaminated by feed iron
- External layer of high density iron rich “glassy” material
- Nodules form on surface of particle
- Diffusional barrier for large feed molecules

Effects of iron poisoning
- Lower conversion
- Increased slurry yield
- Lower Ecat ABD
- Fluidization issues
- Increased SOx

Increasing Iron Levels
Metal Mobility on FCC Catalysts

- Immobile metals: metal level reflects residence time in FCC
  - Exponential decay distribution
  - Nickel
- Mobile metals: present on every catalyst particle
  - Bell curve shaped distribution
  - Vanadium
- *Is iron mobile or immobile under FCC conditions?*
Iron Distribution on Ecat in Various Units

- Iron is mobile under FCC conditions and re-distributes from particle to particle
- Extent of mobility probably determined by temperature, residence time, and type of base catalyst
Can Mobile Iron be Caught in a Trap?

- Capturing mobile iron
  - Removes the nodules on the catalyst outer surface
  - Minimizes the diffusion barrier for large hydrocarbon molecules
CAT-AID Removes Iron Nodules

Ecat iron nodules cured after 1-2 months with CAT-AID

Iron nodules minimized after 4 months despite increase to 1.6 wt% Fe2O3
CAT-AID improves Catalyst Quality

CAT-AID improves catalyst quality by trapping iron:

- Reduces coke
- Reduces dry gas
- Increases gasoline
CAT-AID Commercial Benefits: FCC “A”

- Stopped all flushing Ecat addition
- Conversion increased by 2.3 wt%
- Residue processing and feed CCR increased

<table>
<thead>
<tr>
<th></th>
<th>Base (No CAT-AID)</th>
<th>10% CAT-AID</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue, vol% of Total Feed</td>
<td>3.8</td>
<td>4.7</td>
<td>+24%</td>
</tr>
<tr>
<td>Feed Concarbon, wt%</td>
<td>1.22</td>
<td>1.56</td>
<td>+28%</td>
</tr>
<tr>
<td>Feed Ni+V, ppm</td>
<td>10.2</td>
<td>11.5</td>
<td>+13%</td>
</tr>
<tr>
<td>Fresh Catalyst Addition, TPD</td>
<td>12</td>
<td>12</td>
<td>--</td>
</tr>
<tr>
<td>Flushing Ecat Addition, TPD</td>
<td>12</td>
<td>0</td>
<td>-100%</td>
</tr>
<tr>
<td>CAT-AID Addition, TPD</td>
<td>0</td>
<td>1.2</td>
<td>+1.2</td>
</tr>
<tr>
<td>Conversion, wt%</td>
<td>80.7</td>
<td>83.0</td>
<td>+2.3</td>
</tr>
<tr>
<td>Delta Coke, wt%</td>
<td>0.77</td>
<td>0.72</td>
<td>-0.05</td>
</tr>
</tbody>
</table>
Dry Gas and SOx Benefits: FCC “A”

- Dry Gas yield increase mitigated
  - Ecat metals increased due to discontinuation of flushing Ecat
    - Vanadium increased by 37%
    - Nickel increased by 50%
  - Dry Gas yield increased by only 4%

- CAT-AID also acts as a SOx reduction agent
  - Refinery discontinued use of their SOx reduction additive while SO₂ emissions declined by 88%

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<th>Delta</th>
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<tbody>
<tr>
<td>SOx Reduction Additive, lb/day</td>
<td>100</td>
<td>0</td>
<td>-100%</td>
</tr>
<tr>
<td>Flue Gas SO₂, ppm</td>
<td>250</td>
<td>30</td>
<td>-88%</td>
</tr>
</tbody>
</table>
ZSM-5 Additives for LPG Olefins & Gasoline Octane

Conversion of gasoline range olefins to LPG

- Increase propylene
- Increase butylenes
- Increase iso-butane
- Increase gasoline octane
- Increase liquid volume gain
- No change to dry gas or coke make

Example ZSM-5 Benefits

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<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>+ 2.5 vol%</td>
</tr>
<tr>
<td>Butylenes</td>
<td>+ 1.7 vol%</td>
</tr>
<tr>
<td>Iso-butane</td>
<td>+ 0.8 vol%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>- 3.9 vol%</td>
</tr>
<tr>
<td>Gasoline RON</td>
<td>+ 1.6 RON</td>
</tr>
<tr>
<td>Gasoline MON</td>
<td>+ 0.7 MON</td>
</tr>
</tbody>
</table>

Magnitude of benefits is sensitive to Y-zeolite Rare Earth content
FCC Reaction Pathway

- Cracking in a FCC unit occurs in stages
- ZSM-5 is used to catalyze the cracking of gasoline to LPG
  - Shape selective Zeolite
  - Smaller pores than the base FCC catalyst Y-Zeolite
  - FCC feed molecules are too big to enter - only small diameter gasoline molecules can access the zeolite for cracking
  - Linear pore structure favors cracking of straight chain olefin molecules
- Concentration of ZSM-5 can be adjusted to meet the target gasoline and LPG yields

Separate additive approach provides the most flexibility for optimization and cost minimization
# ZSM-5 Additive Families

<table>
<thead>
<tr>
<th>ZSM-5 Family</th>
<th>Key Benefits</th>
<th>When to Use?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard ZSM-5</td>
<td>• Increase both LPG olefin yield and gasoline octane</td>
<td>• Maximize Alky Rate&lt;br&gt;• Maximize LPG and LCO by combining FCC conversion reduction with ZSM-5&lt;br&gt;• High value outlet for propylene&lt;br&gt;• Maximize liquid volume gain</td>
</tr>
<tr>
<td>High Si/Al Ratio ZSM-5</td>
<td>• Achieve target octane with lower LPG yield than standard ZSM-5</td>
<td>• Tight oil processing: Counteract paraffinic FCC feed impact on gasoline octane&lt;br&gt;• LPG production limited including wet gas compressor, gas plant and/or Alky limits</td>
</tr>
<tr>
<td>Enhanced Activity ZSM-5</td>
<td>• Greater activity for gasoline olefin constrained units</td>
<td>• Maximum propylene production&lt;br&gt;• High concentration of ZSM-5</td>
</tr>
<tr>
<td>ZMX™</td>
<td>• Higher butylene selectivity&lt;br&gt;• Cracks gasoline and heavier</td>
<td>• Value butylene over propylene&lt;br&gt;• Maximize Alky Rate&lt;br&gt;• Maximize liquid volume gain&lt;br&gt;• Convert LCO and Slurry</td>
</tr>
</tbody>
</table>
SUPER Z™ Commercial Benefits: FCC “B”

- Refiner was able to increase propylene and butylene yield at constant conversion
- Conversion was then reduced to maximize both LPG and LCO
SUPER Z Commercial Benefits: FCC “C”

This example demonstrates the benefits of combining SUPER Z with lower Riser temperature:

- Riser Temperature reduced by 33 DegF while maintaining LPG yield
- LPG + LCO yield increased by 1.1 vol%
- Liquid volume yield increased by 2.2 vol%
ISOCAT-HP™: High Si:Al Ratio ZSM-5

- Standard ZSM-5 additives have a Si:Al Ratio in the 30-50 range
- High Si:Al Ratio ZSM-5 has a ratio of 300+
- Increasing the Si:Al ratio reduces the relative rate of cracking compared to isomerization
  - Achieve target octane boost with lower LPG production

Target octane reached with less than 50% incremental LPG production
ZMX for Increased Butylene Selectivity

ZMX is a proprietary zeolite technology supplied by INTERCAT\textsuperscript{JM}

- Higher butylene selectivity compared to standard ZSM-5 additives
- Converts a heavier range of molecules compared to standard ZSM-5

![Graph showing delta yields for dC3=, dC4=, and diC4 for ZCAT-HP and ZMX-BIIP.](image)
INTERCAT$^{JM}$ Addition Systems

- Best Available Loader Technology
  - 350+ loaders installed in FCCs globally
  - Recognized as the Technology Leader
    - Axens, Technip S&W, UOP, CB&I and oil majors
- FCC Catalyst and Additive Loaders
  - Single hopper
  - Multi-compartment hopper
  - Multi-source systems
- Multiple refill options
  - From tote bins, hoppers, containers, bags, trucks
- Worldwide service and support organization
- Most new grass-roots FCCs selecting INTERCAT$^{JM}$ loaders

*Best available technology to enable refiners to control and optimize FCC catalyst addition*
IMS Controller

- INTERCAT\textsubscript{JM} Management System (IMS) Controller
  - Sophisticated PLC control system
  - Simple operator interface
  - Built in alarm and data logging
  - Can operate stand-alone or be controlled from refinery DCS system
Additive Inventory Management (AIM)

- IMS controller securely connects to the Johnson Matthey server.
- Addition rate, alarm data, and additive inventory can be viewed by refiner through password protected website.
- Diagnostic information is available to allow Johnson Matthey technicians to conduct remote troubleshooting.
- 68 loaders currently being tracked on the AIM network worldwide.
  - AIM is an optional feature of INTERCAT JM loaders.

![Additive Inventory Management (AIM) Diagram]
Advanced Design Features

Sintered Metal Filter:

- ~Zero catalyst losses
- Robust self cleaning design - Eliminates the need for unreliable & complex bag house
- Allows vent gases to go straight to atmosphere

Everlasting Valve for catalyst flow control:

- Extremely reliable in catalyst service
- Maintenance frequency > 5 years (valve cycling every 10-20 minutes)
INTERCAT\textsubscript{JM} Addition Systems Benefits

- Improved Accuracy
- Improved Reliability
- Improved Operability
- Improved FCC Profitability

New MSCAS II loaders now available
FCC Additives – Receiving into Refinery

- Tote bins commonly used for FCC additives

- Tote bin management can be challenging for large additive users
Solution for Large Additive Users

- Introducing “Herman’s Hoppers” - 15 ton portable transport silos.
- Silo is transported and placed into position by a specially designed truck.
- Safe and practical solution for medium to large additive consumers
Conclusions

- Shale oil production is impacting FCC operation and optimization
- Johnson Matthey provides multiple additives and addition systems to meet these optimization goals
- Select the best INTERCAT$_{JM}$ additive for your operation

CAT-AID:
Mitigate the impact of Iron and Vanadium Poisoning

ZSM-5:
Increase LPG Olefins & Gasoline Octane

Addition Systems:
Optimize additive handling and addition