Naphtha Catalytic Cracking in FCC Units Past & Present

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Purpose (Objective)

• To present and briefly discuss “light straight run” or paraffinic naphtha catalytic cracking in FCC’s
Contents - Covering 3 Points

Why Naphtha Cracking?

• Feedstock Availability
• How to Crack Naphtha?
• Past & Present (Future) Experiences
Naphtha Sources?

p-Naphtha Sources (no olefins)

• LSR, Natural Gas Condensates, Hydrocracker, Hydrotreater, others?

• Olefinic Naphtha Sources
  • Cracked FCC, Coker, Visbreaker, others?
## Light Crude Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Bakken</th>
<th>WTI</th>
<th>Lite La Sweet</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>Degrees</td>
<td>&gt;41</td>
<td>40</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Wt.%</td>
<td>&lt;0.2</td>
<td>0.33</td>
</tr>
</tbody>
</table>

### Yield Volume %

<table>
<thead>
<tr>
<th>Type</th>
<th>Bakken</th>
<th>WTI</th>
<th>Lite La Sweet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td></td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Naphtha</strong></td>
<td></td>
<td>30</td>
<td>29.8</td>
</tr>
<tr>
<td>Kerosene</td>
<td></td>
<td>15</td>
<td>14.9</td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
<td>25</td>
<td>23.5</td>
</tr>
<tr>
<td>VGO</td>
<td></td>
<td>22</td>
<td>22.7</td>
</tr>
<tr>
<td>Resid</td>
<td></td>
<td>5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Heavy Feeds - Easier to Crack !!

Light Feeds - Hard to Crack !!
Why Naphtha / Condensate? Supply!

- Lighter Crudes for Refinery Feedstocks are Increasing
  - Fracking for Shale Gas and Shale Oil
- Condensates from Natural Gas
- Lighter Crudes Produce More Naphtha
- Increasing Demand for Diesel not Gasoline
- Petrochemicals - Steam Cracking (Feedstock)
  - Ethylene Demand is Growing Faster than Propylene
  - Shifts from Naphtha, Gasoils to Ethane

“Somewhat decoupling” of naphtha pricing from crude
What to Do with Excess Naphtha Supply ??

Dispose It

- Burn it (Fuel)
- Export it for Steam Cracking ????
- Diluent for TAR Sands Production
- Re-inject into Existing Wells

Convert It

- Reformer or Isomerize it
- Crack it
  - Steam Crackers
  - Catalytically Crack It !
Petrochemicals Opportunities

Main Building Blocks

- Olefins - Two Main Blocks
  - Ethylene
  - Propylene
- Butylenes
- Aromatics
  - Benzene
  - Paraxylene (other xylenes too)

* High Olefins - FCC (HOFCC) produces C3= and byproducts of other light olefins and aromatics

Produced by Steam Cracking
Ethane & Liquid Feeds
Naphtha Reformers

Secondary Source Produced by FCC’s

Co-monomer & ALKY Feedstock
## Typical Cracking Yields by Process Type

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>FCC</th>
<th>R2P*</th>
<th>DCC*</th>
<th>HS-FCC*</th>
<th>SC* (C2)</th>
<th>NCC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1-2</td>
<td>1-2</td>
<td>2-6</td>
<td>3-4</td>
<td>45-50</td>
<td>7.1</td>
</tr>
<tr>
<td>Propylene</td>
<td>3-5</td>
<td>10-12</td>
<td>15-25</td>
<td>16-20</td>
<td>1-3</td>
<td>16.8</td>
</tr>
<tr>
<td>Butylenes</td>
<td>6-8</td>
<td>12-14</td>
<td>13-17</td>
<td>13-16</td>
<td>1-2</td>
<td>8.6</td>
</tr>
<tr>
<td>Gasoline</td>
<td>45-55</td>
<td>28-35</td>
<td>22-40</td>
<td>30-40</td>
<td>1-3</td>
<td>48.5</td>
</tr>
</tbody>
</table>

**Legend:**
- **R2P** - Resid to Propylene
- **DCC & HS-FCC** - HOFCC Types
- **SC** – Steam Cracking Ethane
- **NCC** - Naphtha Catalytic Cracking
- **NCC** - Published Data
How to Crack Naphtha?
Cracking Mechanisms

Thermal Cracking
- Non-catalytic Free Radical Chain Formation
- Randomly Ruptures Chemical Bonds

Catalytic Cracking
- Carbenium Ion Formation
- Selectively Opens Chemical Bonds
- Hydrogen Transfer, Isomerization

- Both Form Coke from Condensation
Naphtha Cracking

Steam Cracking - Thermal

- Not Selective to Propylene makes Ethylene (P/E Ratio)
- P/E Ratio of 0.55-0.68 (Naphtha & Gasoil Cracking)
- Steam Cracker capacities are world class size > 1000 KTA

Naphtha Cracking - Catalytic

- Propylene Selective not Ethylene
- P/E Ratio of 1.0 to 2.4
- Naphtha FCC capacities 20 MBPD == 64 KTA of ethylene

SC 20 MBPD = 264 KTA
Steam Cracking Yields

Propylene/Ethylene (P/E) Ratio indicates propylene selectivity

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Ethylene, wt%</th>
<th>Propylene, wt%</th>
<th>P/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>80</td>
<td>3</td>
<td>0.04 (0.0375)</td>
</tr>
<tr>
<td>Propane</td>
<td>44</td>
<td>15</td>
<td>0.34</td>
</tr>
<tr>
<td>Naphtha</td>
<td>30</td>
<td>16</td>
<td>0.53</td>
</tr>
<tr>
<td>Gas oil</td>
<td>23</td>
<td>15</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 1
How to Crack Naphtha?

Lighter Feedstock
- More Heat for Cracking (Higher Heat of Reaction)

Higher Severities
- Higher Reactor Temperatures
- Higher Cat/Oil Ratios
- Increase Residence Times
- Higher Cat Activity
- Different Catalyst Formulations*
How to Crack Naphtha?

Existing Units  Previous Experience  
(Difficult )

Naphtha Feed Injection

• Mix with Current  Feed Injection
• Below Current Feed Injection Elevation
• Into the Reactor Bed  (Bed Cracking)

All Have Issues
Exiting Units  Previous Experience

Mix with Current  Feed Injection

• Increase Cat/Oil (Acts Heat Sink)
• Increase Severity / Conversion **
  (For All Injection Locations)**

Concerns

• Cat Circulation
• Delta Coke Issues
• Octane Loss !!
Exiting Units  Previous Experience

Below Current Feed Injection Elevation

• Hottest Regen Cat Temperature
• Increase Cat/Oil (Acts Heat Sink)
• Claims of Gasoline Sulfur Reduction

Concerns

• Poor Naphtha and Catalyst Mixing
• Potential Coking
• Fresh Feed Catalyst Mixing *
• Inadequate Rx. Residence Times
Exiting Units  Previous Experience

Into the Reactor Bed  (Bed Cracking)

- Increases Residence Time
- Lower Cracking Temperatures
- Non Selective Cracking of Heavy Feed

Concerns

- Units Operate with Bed Cracking  ?
- Method of Injection
How to Crack Naphtha?

Hardware Changes  Revamp / Grassroot Designs

• More Heat for Cracking (Higher Heat of Reaction)
• 2ND Reaction Zone (Riser/Down flow)
• Bed Cracking

Catalyst Changes

• Different FCC & Additive Ratios
• New Catalyst Systems (Grassroots)
Conclusions
Naphtha Catalytic Cracking in FCC Units

- p-Naphtha Supply Sources are Available Both Domestically & Globally
- Crack it! Requires Higher Severities, Rx Temp, C/O, Increase Residence Time, Bed Cracking
- Minimize 450°F+ Content with the Naphtha Feed in the Reaction Zone (Segregate from Heavy Feed)
- Revamps to Existing FCC’s Utilizing a Second Reaction Zone are Feasible (HOFCC’s Technology)
- Cracked Products for Petrochemicals and Alky
Useful References

- “Naphtha Catalytic Cracking for Propylene Production” Dean, C.F. Petroleum Technology Quarter, Processing Shale Feedstocks 2013
- “Optimize Olefins and Aromatics Production”, C.F Dean and W.S. Letzsch, Hydrocarbon Processing, November, 2014
THANK YOU

The End

Questions - Comments ???

Follow-up Discussions?
Advanced Catalytic Olefins (ACO)

- Proprietary KBR proven FCC technology
- P/E ratio $\approx 1$
- Proprietary SK Corporation Catalyst
- Dual Risers
  - Fresh Naphtha
  - Recycle
HS-FCC Naphtha Process

- Retrofit Type to existing FCCU
- Standalone Unit
Aromatics Potential Sources

<table>
<thead>
<tr>
<th></th>
<th>Steam Cracker Gasoline</th>
<th>CCR Reformate</th>
<th>HOFCC Petrochemical Naphtha</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTX Content wt.%</td>
<td>85</td>
<td>56-80</td>
<td>59</td>
</tr>
<tr>
<td>Benzene</td>
<td>56</td>
<td>7-10</td>
<td>6</td>
</tr>
<tr>
<td>Toluene</td>
<td>19</td>
<td>19-28</td>
<td>22</td>
</tr>
<tr>
<td>Total C8’s</td>
<td>9-11</td>
<td>30-42</td>
<td>31</td>
</tr>
</tbody>
</table>

HOFCC naphtha needs further treating, etc. to meet Petrochemical Grade
Ethylene & Propylene Supply Sources

Ethylene Supply Sources
- Ethane: 12%
- Naphtha & Gasoil: 34%
- Propane & Butane: 52%
- Other: 2%

Data Courtesy of IHS CMAI

127 Million Tons (US) 2011*

Propylene Supply Sources
- On Purpose: 30%
- Steam Crackers: 57%
- Refineries: 13%

79 Million Tons (US) 2011*

Data Courtesy of IHS CMAI
Light Crudes & Condensates

- Will be split into Light and Heavy fractions
  - Distillate Cut for Diesel and Jet/Kero
  - Bottoms – GO + Heavy tails for FCC Feed
- LPG

- Naphtha to Petrochemicals not fuels/gasoline*
Boiling Range Distribution of FCC Feed and Products

Wt% FF

C2   C4

Gas   LPG   Naphtha   LCO   Slurry / Feedstock

Boiling Point, °C

PRODUCTS
Principles of Catalysis

- Catalysts lower activation energies of forward & backwards reactions, increasing the rates of both.
- The heat of reaction is unchanged by the catalyst.
- The position of thermodynamic equilibrium is unchanged by the catalyst.
- Non-equilibrium distributions occur under kinetic controlled conditions.
## Summary of Cracking Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>Paraffin + Olefin</td>
</tr>
<tr>
<td>Naphthene</td>
<td>Olefin</td>
</tr>
<tr>
<td>Alkylaromatic</td>
<td>Alkylaromatic + Olefin</td>
</tr>
<tr>
<td>Olefin</td>
<td>Olefin + Olefin</td>
</tr>
</tbody>
</table>

- **Relative Cracking Rates:**
  - Olefin > Alkylaromatic side chain > Paraffin > Naphthene

- Olefins most readily form carbocations

- Aromatic side-chains readily undergo cracking reactions, however, aromatic rings do not crack
Summary of Cracking Reactions

Relative Cracking Rates:

- Olefin > Alkylaromatic side chain > Paraffin > Naphthene
- Olefins most readily form carbocations
- Aromatic side-chains readily undergo cracking reactions, however, aromatic rings do not crack
Full Range Naphtha Yields Olefins wt%
Naphtha Downer vs Steam Cracker Yields

Catalytic Cracking Downer
- Full Range: P/E of 2.4
  - C1: 1.8%
  - C2: 7.1%
  - C3: 16.8%
  - C4: 8.6%
  - Gasoline: 48.5%

Steam Cracking Furnace
- Full Range: P/E of 0.55
  - C1: 14.5%
  - C2: 28.1%
  - C3: 15.5%
  - C4: 4.8%
  - Gasoline: 24.2%

- Light: P/E of 0.55
  - C1: 16.5%
  - C2: 31.1%
  - C3: 17.1%
  - C4: 5.3%
  - Gasoline: 17.4%