Multi-zone Catalytic Cracking: A new platform for Crude to Chemicals in single step

Sukumar Mandal
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MCC Process: Innovative Concepts

- Sequential multi-zone cracking in one riser

- Synergistic combination of Light feedstock (C₄, Naphtha) with Heavy feedstock (CSO, crude) to achieve heat balance

- Utilize exothermic heat of Methanol cracking (optional), taking advantage of cheap and stable price of Methanol

- Utilize high activity stable ZSM-5 of RIL to achieve maximum Propylene and Ethylene; Optimum catalyst formulation for the feedstock to be processed

- Optimum design of each zone variables; zone temp & composition drive closer to equilibrium, allowing high P+E yield in single riser

- Use of all paraffinic + olefinic lighter cut as recycle to MCC riser.

MCC patented based on the above innovative concepts

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Novel feature

• **Feed Flexibility**
  - Olefinic C\textsubscript{4} from FCC/DCU - C\textsubscript{3}/C\textsubscript{4} Splitter bottoms
  - Olefinic naphtha - Light and Heavy Coker Naphtha
  - Straight run naphtha - C\textsubscript{6}/C\textsubscript{7}
  - MCC C\textsubscript{4} and non aromatic naphtha recycle
  - CSO

• **Optional feedstock**
  - FCC Light naphtha
  - Opportunity crude - High TAN, Nitrogen, metals except V
  - Hydrocracker bottom
  - Methanol - attractive feedstock due its cheaper & stable price
  - Customized catalyst formulation for high olefins in product
**Product Flexibility**

- E+P maximization
- E+P+ C₄ olefin maximization
- E+P+C₄ + Gasoline maximization
- Various product objective can be made by varying operating conditions, catalyst composition and feed stock quality

**Processing**

- Sequential multizone cracking in one riser
- Optimized 4 reactor riser zones
- Optimum cracking temperatures, based on feed pre-heat
- Select zone variables to drive cracking process towards equilibrium
- Opportunistic recycle

**Heat balance**

- Synergistic combination of light and heavy feedstock
- Utilize exothermic heat of methanol cracking

⇒ **MCC = FCC of the future**
Methodology

• **ACE**
  - 350+ runs
  - Screening of feed + catalyst

• **Jamnagar pilot plant**
  - 100+ runs
  - High fidelity results mapping commercial Jamnagar FCC performance
  - Multiple feeds, up to 3 co-feeds
  - Optimize operating variable for each MCC zone

• **Catalyst**
  - Customize for feed + operations
  - Tailor to processing + product objectives

• **Demonstration**
  - Proof-of-concept with coker naphtha processing in SEZ FCC
  - Results as predicted by MCC, corrected for constraints

⇒ MCC = Demo-ready
• Optimum cracking temperature: LCN - 620°C & N-Hexane - 675°C
• Need to provide optimum cracking condition depending on the feedstock crackability
• Temp in each zone controlled by feed preheat temp thru feed furnace
• Regen temp & delta coke controlled by heavy fraction feed rate & slurry recycle rate

⇒ Optimize cracking
MCC zones

<table>
<thead>
<tr>
<th>Zone</th>
<th>Temp °C</th>
<th>WHSV, /hr</th>
<th>Severity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>570 – 600</td>
<td>150 – 200</td>
<td>Low</td>
</tr>
<tr>
<td>3</td>
<td>600 – 640</td>
<td>100 – 150</td>
<td>Moderate</td>
</tr>
<tr>
<td>2</td>
<td>630 – 650</td>
<td>50 – 100</td>
<td>High</td>
</tr>
<tr>
<td>1</td>
<td>640 – 680</td>
<td>1 – 10</td>
<td>Super high</td>
</tr>
</tbody>
</table>

• **Riser**
  = Divide in to 4 processing zones
  = Select appropriate feed to route to cracking zones
  = Prevent over-cracking + under-cracking

• **Zone**
  = Dedicated feed injection
  = Feed preheat to control temperature
  = Target desired cracking severity

• **WHSV**
  = Changed with riser dimension + dilution steam-flow
  = Locate appropriate feed injection points

⇒ **MCC = Reactor – Riser with optimal zone cracking**
## Zone Suitability

<table>
<thead>
<tr>
<th>Zone</th>
<th>Feed</th>
<th>Rationale</th>
<th>Severity</th>
<th>Feed Crackability</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Methanol, DME</td>
<td>Light Olefins+ heat balance</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>CSO, Crude, DAO, LR &amp; VR</td>
<td>Light Olefins + heat balance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>VGO, Olefinic naphtha</td>
<td>Easy to crack</td>
<td>L</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Recycle naphtha, Lt SRN, Lt &amp; Hv Condensate/Tight oil</td>
<td>Paraffinic naphtha</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Difficult to crack</td>
<td>H</td>
<td>L</td>
</tr>
</tbody>
</table>

- Segregate feed to match cracking propensity
- Crack VGO + naphtha in a single riser
- Distress Feed streams such as olefinic naphtha
- Feed methanol to match exotherms

⇒ **Ultimate feed cracking flexibility in a single riser**

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In spite of single riser cracking, MCC \( C_3= \) yield is close to thermodynamic equilibrium limit of light olefins, due to

- Higher riser temperature allowing shift of equilibrium and substantial cracking paraffinic naphtha
- Substantial cracking of C4, C5 and higher olefin precursors at the bottom of riser
- Optimum condition for each zone to maximize \( P + E \) depending on crackability of each feed streams
• **Optimized catalyst + additive mix**
  — To cater Feed composition (light : heavy : oxygenate) variation
  — Balance gasoline vs light olefin yield

• **ZSM-5 additive (RIL patented)**
  — More stable formulation with higher P + E
  — Metal modified for lower DG yield

• **Y zeolite catalyst**
  — Heavy feed

• **Catalyst objectives**
  — Minimize dry gas (H₂ & Methane) & coke
  — Maximize C₂=, C₃=, for petrochemicals
  — Maximize C₄= for alky feed /petrochemicals if desirable
  — Maximize BTX for aromatics

⇒ **Tailored catalyst formulation for petrochemical engine**
## Effect of ZSM-5 zeolite stabilization

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>ZSM 5 crystal content, wt.%</td>
<td>B</td>
<td>B</td>
<td>B-10</td>
</tr>
<tr>
<td>Feed</td>
<td>LCN</td>
<td>LCN</td>
<td>LCN</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Catalyst-to-Oil, wt./wt.</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

### Yields, wt.%: ACE data, per pass

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gas(excluding ethylene)</td>
<td>B</td>
<td>-1.5</td>
<td>+0.5</td>
</tr>
<tr>
<td>Ethylene</td>
<td>B</td>
<td>-1.9</td>
<td>+1.3</td>
</tr>
<tr>
<td>Propylene</td>
<td>B</td>
<td>+0.7</td>
<td>+1.2</td>
</tr>
<tr>
<td>LPG</td>
<td>B</td>
<td>-1.6</td>
<td>+2.5</td>
</tr>
</tbody>
</table>

- Compared to commercial additive, RIL’s ZSM 5 additive gives higher yield of light olefins P+E
- Metal doped ZSM 5 additive produces propylene yields comparable to comm add, but additionally reduces yield of ethylene & dry gas.

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MCC vs other catalytic cracking technologies

⇒ MCC = Enormous feedstock flexibility

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MCC Applications = Deeper Integration

**Refinery**
- **Upgrading low value refinery streams** e.g. LCN, HCN, VBN, Condensate, CSO, Resid to high value Petchem feedstock – Light olefins, BTX, Heavy Aromatics.

- **Crude to Olefins** – Direct cracking of crude in one riser, no CDU/VDU/Flashing. Also combined cracking of condensate, shale oil, tight oil etc. along with Crude. About 120 crudes across world have been scanned as suitable for direct processing in MCC.

- **Gasoline Quality** – Limited cracking of Gasoline streams to reduce olefin content while increasing light olefins production.

- **Synergy with Other Bottom Upgradation** Projects e.g. Resid HC and SDA by processing heavier streams produced from these units to light olefins.

**Petchem**
- **MCC integration with SC** – Cracking of SC C₄, C₅-C₈ olefinic raffinates and Py tar in MCC riser while SC can crack C₃ and C₄ paraffins from MCC. In SC, ethane as feed, SC propylene production drops, which can be enhanced easily by adopting MCC.

- **Methanol / DME cracking** in MCC riser & Integrate to SC.
MCC Integration in Refinery

MCC = Max refinery + petrochemical integration
### Comparison of MCC with Steam Cracker

<table>
<thead>
<tr>
<th>Product</th>
<th>LCN</th>
<th>Crude</th>
<th>Lt SRN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCC+</td>
<td>MCC+</td>
<td>SC</td>
</tr>
<tr>
<td>Ethylene</td>
<td>24.8</td>
<td>20.5</td>
<td>34.0</td>
</tr>
<tr>
<td>Propylene</td>
<td>40.5</td>
<td>33.0</td>
<td>18.0</td>
</tr>
<tr>
<td>BTX</td>
<td>18.5</td>
<td>11.5</td>
<td>12.7</td>
</tr>
<tr>
<td>Life cycle cost</td>
<td>B-100~150</td>
<td>B-200~300</td>
<td>B</td>
</tr>
<tr>
<td>Payback, yrs</td>
<td>C-0.5~0.8</td>
<td>C-1~1.5</td>
<td>C</td>
</tr>
</tbody>
</table>

**Economics** Superior economics in MCC arising from following benefits
- MCC handles olefinic feed directly whereas SC requires hydrotreating
- Direct crude cracked in MCC + recycling of naphtha streams in bottom zone of riser, producing higher yield of light olefins
- Lower dry gas yield in MCC (5%) vs SC (18%)
- Good heat balance in MCC, coke from heavy & exothm of methanol, Low feed + Eng cost
- Large scale MCC plant vs multiple furnace in SC => lower capex
=> Strong MCC economics from lower feed price and superior yields
Patents

• **Patents on MCC**
  - Granted : US9550708B2, Australia (2012369895) & Singapore (11201404889T)
  - India : 270880
  - USA : 8685232 (two zone)
  - Pending : in Japan & Europe

• **Patent on FCC additives**
  - India : 268048
  - USA : 9067196
  - Japan : 2014-520792
  - Nigeria : NG/C/2014/013

• **Patent on Enhanced Propylene & LPG Recovery**
  - USA : 8618344

⇒ **Full Freedom to Operate (FTO) for MCC**
Conclusion

— MCC is a new process developed for cracking of diverse hydrocarbon streams in sequential manner in a single riser to make substantial
  ▪ Propylene (> 30wt %)
  ▪ and Ethylene (>18wt %)
  ▪ BTX (15%).
— This is alternate to SC, but for feedstock, SC can not handle
Thank You