Fluidized Catalytic Cracking

Chapter 6
Overview of Catalytic Cracking

FCC “heart” of a modern US refinery

- Nearly every major fuels refinery has an FCCU

One of the most important & sophisticated contributions to petroleum refining technology

Capacity usually 1/3 of atmospheric crude distillation capacity

Contributes the highest volume to the gasoline pool

EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/
U.S. Refinery Implementation

EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinercapacity/
Purpose

Catalytically crack carbon-carbon bonds in gas oils

- Fine catalyst in fluidized bed reactor allows for immediate regeneration
- Lowers average molecular weight & produces
- High yields of fuel products
- Produces olefins

Attractive feed characteristics

- Small concentrations of contaminants
  - Poison the catalyst
- Small concentrations of heavy aromatics
  - Side chains break off leaving cores to deposit as coke on catalyst
  - Must be intentionally designed for heavy resid feeds

Products may be further processed

- Further hydrotreated
- Olefins used as feedstock to alkylation process
Large conversion to light products requires some coke formation

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000
What is a fluidized bed?

https://www.youtube.com/watch?v=3BqVFGCUviY

http://www.youtube.com/watch?v=EB0r6A5VxFU
Fluid Catalytic Cracker

http://flowexpertblog.com/2013/09/05/fccu-in-todays-refineries/

http://www.secinfo.com/dsvrp.uEe6.d.htm#1stPage
Typical FCC Complex

Figure modified from Koch-Glitsch Bulletin KGSS-1, Rev. 3-2010, http://www.koch-glitsch.com/Document%20Library/KGSS.pdf
FCC Riser/Regenerator Combination

“Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis”
CFD Simulation of an FCC Riser

https://www.youtube.com/watch?v=_781g72wCQM
History – Fixed, Moving, & Fluidized Bed Cracking

Cyclic fixed bed catalytic cracking commercialized in late 1930s

- 1st Houdry Process Corporation catalyst cracker started up at Sun Oil’s Paulsboro, New Jersey, refinery in June 1936
- Three fixed bed reactors & processed 2,000 barrels/day
- Other adoptees: Sun, Gulf, Sinclair, Standard Oil of Ohio, & The Texas Company

Sun & Houdry started developing moving bed process in 1936

- 1st commercial 20,000-barrel/day unit commissioned at Magnolia’s Beaumont Refinery in 1943

Fluidized bed catalytic cracking

- Up-flow dense phase particulate solid process credited to W.K. Lewis, MIT
- Early adopters: Standard Oil of New Jersey, Standard Oil of Indiana, M.W. Kellogg, Shell Oil, The Texas Company, & others
- Dense phase – back mixed reactor
- Model I FCCU at Standard Oil of New Jersey’s Baton Rouge Refinery, 1942
- Model II dominated catalytic cracking during early years

Dilute phase — riser reactor design

- Molecular sieve based catalysts – 1960s
- Significantly higher cracking activity & gasoline yields – lower carbon on catalyst
- Plug flow – drastically reduced residence time & 90% feed conversions
FCC Feedstocks

Chemical species considerations

- Aromatic rings typically condense to coke
  - Feedstock can be hydrotreated to reduce the aromatic content
  - Amount of coke formed correlates to carbon residue of feed
    - Feeds normally 3-7 wt% CCR
- Catalysts sensitive to heteroatom poisoning
  - Sulfur & metals (nickel, vanadium, & iron)
  - Feeds may be hydrotreated to reduce poisons

Atmospheric & vacuum gas oils are primary feeds

- Could be routed to the hydrocracker for diesel production
  - Not as expensive a process as hydrocracking
- Dictated by capacities & of gasoline/diesel economics

Hydrotreated feed results in cleaner, low-sulfur products

- If feedstock not hydrotreated then the products must be separately hydrotreated to meet ultra low sulfur specs
FCC Products

Primary goal – make gasoline & diesel, minimize heavy fuel oil production
- “Cat gasoline” contributes largest volume to the gasoline pool
  - Front-end rich in olefins, back-end aromatics
  - Does not contain much C-6 & C-7 olefins – very reactive & form lighter olefins & aromatics

Coke production relatively small but very important
- Burned in regenerator & provides heat for cracking reactions
- Largest single source of CO2 in refinery

Light ends high in olefins
- Good for chemical feedstock
- Can recover refinery grade propylene
- Propylene, butylene, & C5 olefins can be alkylated for higher yields of high-octane gasoline

Cat kerosene & jet fuel – rarely made
- Low cetane number because of aromatics – lowers quality diesel pool
- Poor cold properties

Gas oils – “cycle oils”
- Essentially same boiling range as feedstock

“Slurry”
- Heavy residue from process
- High in sulfur, small ring & polynuclear aromatics, & catalyst fines
- Usually has high viscosity
- Disposition
  - Blended into the heavy fuel oil (“Bunker Fuel Oil” or Marine Fuel Oil)
  - Hydrocracked
  - Blended into coker feed – can help mitigate shot coke problems
Product Yields

Produces high yields of liquids & small amounts of gas & coke

- Mass liquid yields are usually 90% – 93%; liquid volume yields are often more than 100% (volume swell)
- (Rule of thumb) Remaining mass yield split between gas & coke

The yield pattern is determined by complex interaction of feed characteristics & reactor conditions that determine severity of operation

- Rough yield estimation charts given in text pp. 117 – 130 & pp. 144-156

Conversion (per the text book) defined relative to what remains in the original feedstock boiling range:

\[
\% \text{ Product Yield} = 100 \times \frac{\text{Product Volume}}{\text{Feed Volume}} \\
\text{Conversion} = 100\% - (\% \text{ Cycle Oil Yield})
\]
# FCCU Yield Example

## Product Yields from FCCU Using Gary et. al. Correlations

Conversion = 72.0 vol%

<table>
<thead>
<tr>
<th>Fraction</th>
<th>bbl/day</th>
<th>lb/day</th>
<th>Yields vol%</th>
<th>Yields wt%</th>
<th>Standard Densities</th>
<th>Watson K Factor</th>
<th>Sulfur Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCCU Feed (Total Gas Oil)</td>
<td>25,000</td>
<td>7,915,013</td>
<td>100.0%</td>
<td>100.0%</td>
<td>25.00</td>
<td>0.9042</td>
<td>7.538</td>
</tr>
<tr>
<td>Light gases (C2-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane (C3)</td>
<td>639</td>
<td>113,468</td>
<td>2.56%</td>
<td>1.43%</td>
<td>147.6</td>
<td>0.5070</td>
<td>4.227</td>
</tr>
<tr>
<td>Propylene (C3=)</td>
<td>1,451</td>
<td>264,749</td>
<td>5.80%</td>
<td>3.34%</td>
<td>140.1</td>
<td>0.5210</td>
<td>4.344</td>
</tr>
<tr>
<td>Iso-butane (IC4)</td>
<td>1,397</td>
<td>275,362</td>
<td>5.59%</td>
<td>3.48%</td>
<td>119.9</td>
<td>0.5629</td>
<td>4.693</td>
</tr>
<tr>
<td>n-butane (NC4)</td>
<td>491</td>
<td>100,375</td>
<td>1.96%</td>
<td>1.27%</td>
<td>110.8</td>
<td>0.5840</td>
<td>4.869</td>
</tr>
<tr>
<td>Butylene (C4=)</td>
<td>1,902</td>
<td>400,492</td>
<td>7.61%</td>
<td>5.06%</td>
<td>103.8</td>
<td>0.6013</td>
<td>5.013</td>
</tr>
<tr>
<td>Gasoline (C5+)</td>
<td>14,263</td>
<td>3,732,025</td>
<td>57.05%</td>
<td>47.15%</td>
<td>57.9</td>
<td>0.7473</td>
<td>6.230</td>
</tr>
<tr>
<td>Light Cycle Oil (LCO)</td>
<td>5,300</td>
<td>1,630,520</td>
<td>21.20%</td>
<td>20.60%</td>
<td>29.6</td>
<td>0.8786</td>
<td>7.325</td>
</tr>
<tr>
<td>Heavy Cycle Oil (HCO)</td>
<td>1,700</td>
<td>620,576</td>
<td>6.80%</td>
<td>7.84%</td>
<td>4.2</td>
<td>1.0425</td>
<td>8.692</td>
</tr>
<tr>
<td>Coke</td>
<td>387,452</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total: 27,143 7,915,013 108.57% 100.00%

Cycle Oils: 7,000 2,251,096 28.00% 28.44%

Total LPG: 5,880 1,154,446 23.52% 14.59%

<table>
<thead>
<tr>
<th>Sulfur Distribution Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>3.90%</td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>0.06%</td>
</tr>
<tr>
<td>0.43%</td>
</tr>
<tr>
<td>0.86%</td>
</tr>
<tr>
<td>2.58%</td>
</tr>
<tr>
<td>39,575</td>
</tr>
<tr>
<td>0.55%</td>
</tr>
<tr>
<td>0%</td>
</tr>
</tbody>
</table>

## Yields [vol%]

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yields [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unnormalized</td>
<td>Normalized</td>
</tr>
<tr>
<td>----------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Propane (C3)</td>
<td>2.92% 2.56%</td>
</tr>
<tr>
<td>Propylene (C3=)</td>
<td>6.63% 5.80%</td>
</tr>
<tr>
<td>Iso-butane (IC4)</td>
<td>6.38% 5.59%</td>
</tr>
<tr>
<td>n-butane (NC4)</td>
<td>2.24% 1.96%</td>
</tr>
<tr>
<td>Butylene (C4=)</td>
<td>8.69% 7.61%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>26.87% 23.52%</strong></td>
</tr>
</tbody>
</table>
Boiling Point Ranges for Products

Based on example problem in:
Gerald Kaes, Athens Printing Company, 2004

Updated: July 1, 2019
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Catalytic Cracking Catalysts & Chemistry

Composites – zeolite dispersed in amorphous matrix

- Zeolite – 10-50 wt % – provides activity, stability, & selectivity
- Matrix – 50-90% – provides desirable physical properties & some catalytic activity

Acid site catalyzed cracking & hydrogen transfer via carbonium mechanism

- Basic reaction — carbon-carbon scission of paraffins & cycloparaffins to form olefins & lower molecular weight paraffins & cycloparaffins

  Paraffin $\rightarrow$ Paraffin + Olefin
  Alkyl Naphthene $\rightarrow$ Naphthene + Olefin
  Alky Aromatic $\rightarrow$ Aromatic + Olefin

- Example

  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}=\text{CHCH}_3$

- Olefins exhibit carbon-carbon scission & isomerization with alkyl paraffins to form branched paraffins
- Cycloparaffins will dehydrogenate (condense) to form aromatics
- Small amount of aromatics & olefins will condense to ultimately form coke
"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
Catalysts & Chemistry

FCC catalysts consists of a number of components to meet demands of FCC system

- High activity, selectivity, & accessibility; coke selectivity
  - High gasoline & low coke yields
- Good fluidization properties & attrition resistance
  - Size between flour & grains of sand.
  - Balance between strength (so it doesn’t break apart as it moves through system) but doesn’t abrade the equipment internals.
    - 70 tons/min typical circulation rate
- Hydrothermal stability
- Metals tolerance

Main active component is a zeolite

- Internal porous structure with acid sites to crack larger molecules to desired size range

“Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis”
Catalysts & Chemistry

Research continues by catalyst suppliers & licensors

- Recognition that both crackability of feed & severity of operations are factors
- Theoretical basis for cracking reactions lead to more precise catalyst formulation
- Catalyst tailored to maximize a particular product
  - Focus used to be on gasoline...
  - now more likely diesel yield or ...
  - increased olefin production
- Additives
  - Bottoms cracking
  - ZSM-5 for increased C3 production
  - CO combustion promoters in regenerator

FCC catalyst cost

- Generally the 2nd highest operating expense, after crude oil purchases
- May pay upwards of $3,000 per ton

“Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis”
Yields are catalyst dependent

<table>
<thead>
<tr>
<th>As Produced Yields, volume %</th>
<th>Base</th>
<th>HDXtra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>56.9</td>
<td>51.5</td>
</tr>
<tr>
<td>LCO</td>
<td>20.7</td>
<td>30.9 (+10.2%)</td>
</tr>
<tr>
<td>CS0</td>
<td>5.7</td>
<td>5.1</td>
</tr>
<tr>
<td>Corrected LCO (430–650°F) vol %</td>
<td>16.8</td>
<td>20.8 (+4%)</td>
</tr>
</tbody>
</table>

*Table 1: FCC unit yield data of first commercial trial of HDXtra at Frontier, El Dorado, KS*

*Figure 3: Bottoms upgrading of commercial FCC catalyst matrix materials in comparison to the novel Prox-SMZ matrix.*

*Figure 5: Defining the project objective for the development of Stamina*

*Updated: July 1, 2019
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New Resid Fluid Catalytic Cracking (FCC) Catalyst Technology for Maximum Distillates Yield Demonstrated in Big West Oil’s Salt Lake City Refinery, BASF Technical Note
Operating Conditions & Design Features

Designed to provide balance of reactor & regenerator capabilities

Usually operate to one or more mechanical limits

- Common limit is capacity to burn carbon from the catalyst
  - If air compressor capacity is limit, capacity may be increased at feasible capital cost
  - If regenerator metallurgy is limit, design changes can be formidable.
  - Regenerator cyclone velocity limit

- Slide valve $\Delta P$ limit
FCC Riser/Regenerator Combination

Risers

- Inlet typically 1300°F, outlet 950 – 1000°F
- Increased reactor temperature to increase severity & conversion
  - May need to reverse to lower olefin content (gasoline formulation regulations)
- Reactor pressure controlled by the fractionator overhead gas compressor
  - Typically 10 to 30 psig
- High gas velocity fluidizes fine catalyst particles.
- Current designs have riser contact times typically 2 to 3 seconds.
- Important design point: quick, even, & complete mixing of feed with catalyst
  - Licensors have proprietary feed injection nozzle systems to accomplish this
  - Atomize feed for rapid vaporization
  - Can improve performance of an existing unit

Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007
FCC Riser/Regenerator Combination

Cyclones
- Gas/solid separation in cyclones
  - Increased cross sectional area decreases gas velocity.
  - Normally 2 stage cyclones.
- Rapid separation to prevent “over cracking.”

Regenerators
- Regenerators operate 1200 – 1500°F
  - Limited by metallurgy or catalyst concerns
- Temperature determines whether combustion gases primarily CO or CO₂
  - Partial Burn. Under 1300°F. High CO content. Outlet to CO boilers & HRSG (heat recovery/steam generation).
  - Full Burn. High temperatures produce very little CO. simpler waste heat recover systems.

Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007
FCC Riser/Regenerator Combination

Heat balance

- Reactor & regenerator operate in heat balance
  - More heat released in the regenerator, higher temperature of regenerated catalyst, & higher reactor temperatures.
- Heat moved by catalyst circulation.
Resid Catalytic Cracking

Economics favoring direct cracking of heavier crudes & resids

- Instead of normal 5-8% coke yield can reach 15% with resid feeds

Requires heat removal in regenerator

- “Catalyst coolers” on regenerator to
  - Produces high-pressure steam
  - Specially designed vertical shell & tube heat exchangers
- Proprietary specialized mechanical designs available with technology license
Summary
Summary

Heart of a gasoline-oriented refinery

Catalytically cracks feedstocks that are too heavy to blend into the diesel pool

- Special designs required to crack resid

Extremely active catalyst systems

- Deactivate with coke in the matter of seconds
- Requires the use of fluidized bed systems to regenerate catalyst
- The heat liberated from burning off the coke provides the heat to drive the cracking reactions
Supplemental Slides
FCCs tend to be less expensive than Hydrocrackers

- 50,000 bpd distillate FCC – $150 million installed cost
- 50,000 bpd @ 2000 scf/bbl – $350 million installed cost
## Fluidized Catalytic Cracking Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axens</td>
<td>Resid cracking</td>
</tr>
<tr>
<td>ExxonMobil Research &amp; Engineering</td>
<td>Fluid catalytic cracking</td>
</tr>
<tr>
<td>Haldor Topsoe A/S</td>
<td>Fluid catalytic cracking – pretreatment</td>
</tr>
<tr>
<td>KBR</td>
<td>Fluid catalytic cracking; FCC – high olefin content; resid cracking</td>
</tr>
<tr>
<td>Lummus Technology</td>
<td>Fluid catalytic cracking; FCC for maximum olefins</td>
</tr>
<tr>
<td>Shaw</td>
<td>Fluid catalytic cracking; deep catalytic cracking; resid cracking</td>
</tr>
<tr>
<td>Shell Global Solutions</td>
<td>Fluid catalytic cracking</td>
</tr>
<tr>
<td>UOP</td>
<td>Fluid catalytic cracking</td>
</tr>
</tbody>
</table>
Other FCC Configurations

Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007
Other FCC Configurations

Exxon Flexicracking IIR FCC Unit

M.W. Kellogg Design

Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

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Catalyst Considerations

Adjustment of active catalytic components (zeolite & active matrix) can achieve various refinery objectives

Considerations

- Bottoms Cracking
- Octane
- Coke selectivity
- ZSM-5 additive
- Resid cracking
- Additives
- FCC catalyst cost
  - Generally the 2nd highest operating expense, after crude oil purchases
  - May pay upwards of $3,000 per ton

FCC Catalyst Selection Considerations, Hoyer, March 2015
http://www.refinerlink.com/blog/FCC_Catalyst_Selection_Considerations/
Catalyst Considerations

Bottoms Cracking

- Large-pore matrix permits easy access of large molecules
- Large molecule cracking mechanisms
  - Matrix cracking
    - Most efficient upgrading into higher-valued gasoline & light cycle oil
  - Cracking on the external zeolite surface
    - Minimal bottoms upgrading, very small fraction of total zeolite surface
  - Thermal cracking
    - Nonselective – tends to produce gas & coke

Octane

- Sodium content & amount of rare earth exchange effects degree of octane enhancement
- Trade offs
  - Increased FCC conversion & gasoline yield can be at the expense of octane number
  - Increased gasoline olefin content can improve RON
  - Increased branching & aromatic content improves MON
Catalyst Considerations

Coke selectivity

- A coke-selective catalyst reduces the regenerator temperature
  - Could allow for a higher reactor temperature to increase octane w/o exceeding regenerator temperature or air compressor limits

ZSM-5 additive

- Does not require complete catalyst change out – small amount, 1-5% of total catalyst
- Enhances gasoline octane
  - Selectively cracks straight chain paraffins & olefins (low-octane) to mainly C3 and C4 olefins.
  - Some olefins isomerized to more highly branched (high octane)
  - Does not affect aromatics or naphthenes (high octane)
Catalyst Considerations

Resid cracking

- No single optimum catalyst for all resid processing applications
- Allow for greater selectivity in products compared to thermal cracking
  - Must cope with high levels of coke precursors & metals in resid feeds
- Requires coke-selective & metals-resistant catalysts, metals passivators, and SOx emission-reducing catalysts
- Feed’s CCR issues w/o cat cooler
  - Increased CCR, increased regenerator temperature, decreased C/O ratio, & declining conversion

Additives

- Passivation agents to mitigate nickel and vanadium
- SOx-reduction additives for regenerator emissions
- High-density fines used as fluidization aids.
Improving Cat Cracking Process Monitoring

Mass Balance
- Hydrocarbon balance – can you account for your process stream?
- Catalyst balance – Can you account for every pound of catalyst from injection to regenerator spent catalyst to slurry catalyst content?

Pressure Balance
- Drives reliability & long-term safe operation
- Understand pressure profiles including: air blower, regenerator, reactor, & wet gas compressor
- Help troubleshoot mechanical issues –air grids & cyclones

Heat Balance
- Important for kinetic reactions of the plant as well as distillation and heat recover/integration in the unit

Yield Balance
- Understand the economic implications of the unit & help focus on key indicators
- Catalyst cost/usage impacts the operating expense of the Cat Cracker?
- Impact of feed quality variations on yields?

Ref: http://www.refinerlink.com/blog/Cat_Cracking_Process_Monitoring