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, 2016 database, published June 2016
http://www.eia.gov/petroleum/refinerycapacity/
U.S. Refinery Implementation

EIA, Jan. 1, 2016 database, published June 2016
http://www.eia.gov/petroleum/refinerycapacity/
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 hydrocracked
  - Alkylated to improve gasoline anti-knock properties

Figure: http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html
Characteristics of Petroleum Products

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
Typical FCC Complex
FCC Riser/Regenerator Combination

"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
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

- Considerations due to chemical species
  - Aromatic rings typically condense to coke
    - No hydrogen added to reduce coke formation
    - 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

- 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 products, not high in sulfur
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 small but very important
  - Burned in regenerator & provides heat for cracking reactions
- 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
  - Low cetane number because of aromatics – lowers quality diesel pool
- 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 defined relative to what remains in the original feedstock boiling range

\[
\% \text{ Product Yield} = 100 \times \frac{\text{(Product Volume)}}{\text{(Feed Volume)}}
\]

Conversion = 100% - (% Cycle Oil Yield)
# FCCU Yield Example

## Product Yields from FCCU

### Operation Info:

Conversion = **72.0** vol%

<table>
<thead>
<tr>
<th>Fraction</th>
<th>bbl/day</th>
<th>lb/day</th>
<th>vol%</th>
<th>wt%</th>
<th>°API</th>
<th>SpGr</th>
<th>lb/gal</th>
<th>wt%</th>
<th>lb/day</th>
<th>wt%</th>
<th>°API</th>
<th>SpGr</th>
<th>lb/gal</th>
<th>wt%</th>
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</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>25.0</td>
<td>0.9042</td>
<td>7.538</td>
<td>12.00</td>
<td>0.50</td>
<td>39,575</td>
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<td></td>
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<td>Light gases (C2-)</td>
<td>389,994</td>
<td>4.93%</td>
<td>2.5%</td>
<td>113,468</td>
<td>24.9%</td>
<td>9,846</td>
<td>2.5%</td>
<td>147.6</td>
<td>0.5070</td>
<td>4.227</td>
<td>1.1%</td>
<td>3,027</td>
<td>7.6%</td>
<td>2.7%</td>
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<tr>
<td>Propane (C3)</td>
<td>639</td>
<td>113,468</td>
<td>2.5%</td>
<td>1.43%</td>
<td>140.1</td>
<td>0.5210</td>
<td>4.344</td>
<td>1.1%</td>
<td>3,027</td>
<td>7.6%</td>
<td>1.1%</td>
<td>3,027</td>
<td>7.6%</td>
<td>1.1%</td>
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<td>Propylene (C3=)</td>
<td>1,451</td>
<td>264,749</td>
<td>5.80%</td>
<td>3.34%</td>
<td>119.9</td>
<td>0.5629</td>
<td>4.693</td>
<td>3.0%</td>
<td>3,027</td>
<td>7.6%</td>
<td>3.0%</td>
<td>3,027</td>
<td>7.6%</td>
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<td>Iso-butane (IC4)</td>
<td>1,397</td>
<td>275,362</td>
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<td>3.48%</td>
<td>110.8</td>
<td>0.5840</td>
<td>4.869</td>
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<td>3,027</td>
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<td>n-butane (NC4)</td>
<td>491</td>
<td>100,375</td>
<td>1.96%</td>
<td>1.27%</td>
<td>104.1</td>
<td>0.6005</td>
<td>5.006</td>
<td>1.0%</td>
<td>3,027</td>
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<td>Butylenes (C4=)</td>
<td>1,902</td>
<td>399,959</td>
<td>7.61%</td>
<td>5.05%</td>
<td>601</td>
<td>0.6005</td>
<td>5.006</td>
<td>4.9%</td>
<td>3,027</td>
<td>7.6%</td>
<td>4.9%</td>
<td>3,027</td>
<td>7.6%</td>
<td>4.9%</td>
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<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>
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<td>6.230</td>
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<td>0.1%</td>
<td>2,010</td>
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<tr>
<td>Light Cycle Oil (LCO)</td>
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<td>28.45%</td>
<td>29.5</td>
<td>0.8789</td>
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<td>6,095</td>
<td>15.4%</td>
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<td>6,095</td>
<td>15.4%</td>
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<td>Heavy Cycle Oil (HCO)</td>
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<td>7.84%</td>
<td>4.2</td>
<td>1.0425</td>
<td>8.692</td>
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<td>396</td>
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<td>Coke</td>
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<td>28.57%</td>
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</table>

<table>
<thead>
<tr>
<th>Product Yields from FCCU</th>
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<tbody>
<tr>
<td><strong>Total</strong></td>
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<tr>
<td>Cycle Oils</td>
</tr>
<tr>
<td>Total LPG</td>
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</table>

<table>
<thead>
<tr>
<th>Yields [vol%]</th>
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<tbody>
<tr>
<td><strong>Fraction</strong></td>
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<tr>
<td><strong>Unnormalized</strong></td>
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<tr>
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<tr>
<td>Butylenes (C4=)</td>
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<td>Total</td>
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Boiling Point Ranges for Products

Kaes's Example FCC Problem

![Boiling Point Ranges for Products](image-url)
Catalysts & Chemistry

• 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 —→ Paraffin + Olefin
  Alkyl Naphthene —→ Naphthene + Olefin
  Alkyl Aromatic —→ Aromatic + Olefin

• Example

  \[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH} = \text{CHCH}_3\]

  ▶ 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 consist 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

"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
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 ΔP 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 & resid feeds
  - Normally 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

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Summary

- Heart of a gasoline-oriented refinery
- Catalytically cracks feedstocks that are too heavy to blend into the diesel pool
  - Special designs required to attempt to crack resid
- Cat naphtha good properties for gasoline blending
  - High olefin content leads to good octane rating
- Lighter materials can be separated for petrochemical feedstocks
- 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

- FCC installed cost
- Fluidized catalytic cracking technology providers
- Other RCC configurations
- Improving Cat Cracking Process Monitoring
FCC vs. Hydrocracker Installed Cost

- 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

**FIGURE 6.28** Fluid catalytic cracking units investment cost: 2005 U.S. Gulf Coast (see Table 6.5).

**FIGURE 7.7** Catalytic hydrocracking unit investment cost: 2005 U.S. Gulf Coast (see Table 7.4).
# Fluidized Catalytic Cracking Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
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<tbody>
<tr>
<td>Axens</td>
<td>Resid cracking</td>
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<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>
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<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
Improving Cat Cracking Process Monitoring

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

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

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

- **Yield Balance**
  - β 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](http://www.refinerlink.com/blog/Cat_Cracking_Process_Monitoring)