FCC Resid Cracking

E. Thomas Habib, Jr.

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Overview

- Resid Cracking Basics
- Example – Pilot Plant Study
- Issues
- Resid Catalyst Design
  - Zeolite Unit Cell Size (UCS)
  - Zeolite Mesoporosity and Extra-framework alumina
  - Matrix Pore Structure
  - Ni Tolerance
  - V Tolerance
- Grace Resid Catalysts - Genesis®
Resid Cracking Basics (continued)

- Resid cracks rapidly (due to high MW) but:
- \( \Delta \) Coke is high (raises regenerator temperature) which lowers Cat/Oil ratio.
- Metals from the resid poison the catalyst:
  - Increasing molecular \( H_2 \) yield,
  - Further increasing \( \Delta \) coke,
  - And deactivating the catalyst (higher additions required to maintain activity).
- Usually low feed temperature and/or catalyst coolers are needed (or the heat balance will force a very unattractive operation).
- Catalyst Coke Selectivity is Critical.
## Feed Properties

<table>
<thead>
<tr>
<th></th>
<th>Base Feed</th>
<th>Atm Resid</th>
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</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>22.4</td>
<td>17.8</td>
</tr>
<tr>
<td>K Factor</td>
<td>11.67</td>
<td>11.64</td>
</tr>
<tr>
<td>CCR, wt%</td>
<td>0.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>0.2</td>
<td>11.9</td>
</tr>
<tr>
<td>V, ppm</td>
<td>0.2</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Resid Cracking Study

(DCR Pilot plant data)

Delta Coke vs. Atm Bottoms in Feed

Delta Coke, wt% vs. Atm Bottoms in Feed, vol%
Resid Cracking Study

(DFR Pilot plant data)

Resid Feed Study

Approximately 0.2 wt% conversion loss for every 1 vol% ATB in feed.

\[ y = -0.2139x + 71.877 \]

\[ R^2 = 0.9777 \]

Data interpolation at 4 wt% coke

Long term effects are expected to be more severe as e-cat metals increase.
Resid Cracking Study
(DCR Pilot plant data)

Gasoline Yield vs. % Atm Bottoms in Feed

Atm Bottoms in Feed, vol% vs. Gasoline Yield, wt%
• Ni and V appear in the resid fractions as metal complexes.

• Fe can appear as “tramp Fe” – small particles of steel that have minimal effect, or as highly detrimental organic Fe.

• Na is usually from salt water (poor de-salting).

• Other metals are rare and can usually be traced to feeds slops (lube extracts, fuel additives, or catalyst fines from upstream processes).
For FCCUs with high catalyst addition rate relative to the total inventory, Ni tends to accumulate on the surface. However, given enough time in the unit, Ni can distribute uniformly throughout the particle.

*Ni distribution on ECAT also depends on catalyst technology employed.*
Both Na and V distribute uniformly on ECAT particles.
Nickel and Vanadium – Which is Worse?

- Both Ni and V are dehydrogenation catalysts and will degrade valuable products to coke and H₂.
- Ni is ~ 4 times as active for hydrogen formation as V.

Ni Equivalent = Ni + V/4 – 1.21*Sb

- Ni can be passivated with Sb or Bi (maximum Sb pickup varies with catalyst and Ni level).
- Ni tolerant FCC catalysts are available.
- Ni is most detrimental under reducing conditions (partial burn regeneration).
Vanadium

- V (unlike Ni) destroys zeolite and lowers activity.

- V (unlike Ni) is mobile and moves from catalyst particle to other catalyst particles.

- V is most detrimental when oxidized (full burn regeneration).

- V can be mitigated by catalyst V-traps.

Net: High V is usually a bigger problem.
Conradson Carbon Residue (CCR)

Also called Concarbon

- CCR is a thermal destruction lab test that gives an indication of the direct coking tendency of the feed.
- Typically, between 30% and 100% of CCR will go to coke, independent of conversion level.
- Typical CCR:
  - < 0.5% for VGO
  - Up to 9% for resid feeds.
- Major impact on FCC operations via heat balance,
  - increases regenerator temperature,
  - lowers Cat/Oil, and
  - lowers conversion.
Other Impurities – Nitrogen & Sulfur

- Nitrogen and Sulfur levels tend to be higher for resid feeds than gas oil feeds.

- Hydrotreating the feed (or products) can greatly lower the levels, particularly for Sulfur.

- Nitrogen –
  - Absorbs on the catalyst sites, deactivating those sites until the N is burned off in the regenerator, and increasing coke.
  - About 50% of feed N appears in coke.

- Sulfur –
  - Appears in all FCC product streams and is distributed according to the feed origin and pre-treatment.
  - Little effect on conversion and yields, but:
  - Has a major effect on operations due to emission regulations and fuel specifications.

- Sulfur in gasoline and regenerator flue gas (SO\textsubscript{x}) can be minimized by use of special FCC catalysts and additives.
FCC Resid Catalyst Design

- **Resid Catalyst Requirements:**
  - Coke selectivity
  - Bottoms cracking
  - Stability

- **Design Control Features:**
  - Zeolite Unit Cell Size (UCS)
  - Zeolite Extraframework Alumina and Mesoporosity
  - Matrix Activity and Pore Structure
  - Ni Traps
  - V Traps
Effect of USC on Coke Selectivity

unit cell size range for minimum coke ca. 24.28 - 24.34 Å
Role of Mesopores:
- Increases the diffusivity of hydrocarbon molecules to the interior of the zeolite.
- Provides additional matrix surface area for bottoms cracking.
N2 PSD of Al Sol Catalysts with Varying UCS

Mesopore volume increases with increasing level of dealumination

CPS with 3000ppm V + 2000ppm Ni

Pore Volume (cc/g)

- 24.24 Å
- 24.31 Å
- 24.36 Å
- 24.41 Å
- 24.45 Å

Pore Diameter (Å)
Role of Extra-framework Alumina

- Initiates cracking reactions
  - Strong Lewis acid sites
  - Together with Framework Alumina, form Super Bronsted acid sites
- Provides Matrix Activity for Bottoms Cracking
Extra-framework Alumina Increases Activity

Kinetics of n-Hexane Cracking

Turnover Rate (molecule/site s x10^5)

470 480 490 500 510 520 530 540 550

Reaction Temperature/C

High Extraframework Al2O3

Low Extraframework Al2O3

Hydrothermal Dealumination Chemical Dealumination

Data from Kung et al., Catal Today, 52 (1999) 91
Role of FCC Matrix

- Provides pore structure to allow feed molecules to diffuse in and product molecules to diffuse out of the catalyst.

- Helps crack the large molecules to provide ‘feed’ for the zeolite component.

- Active for cracking naphthenoaromatic compounds.

- Important for metals tolerance.
Bottoms Cracking Mechanism

Ref., Zhao et al, AM-02-52

Type I - Precracking and Feed Vaporization
Type II - Dealkylation of alkyl aromatics
Type III - Conversion of naphthenoaromatics

Type I - matrix dependent
Type II - zeolite dependent
Type III - matrix dependent
Matrix Activity Can Improve Coke Selectivity

Matrix activity is combination of porosity and number of acid sites

Coke to bottoms selectivity advantage of high matrix activity alumina-sol increases with increasing amount of resid in the feedstock.
Configuration Diffusion:

\[ D_{\text{eff}} = D_{\text{bulk}} \left(1 - \frac{d_{\text{molecule}}}{d_{\text{pore}}}\right)^4 \]  
(Spry et al, 1975)

- Heavy feed molecules are of the size range 10 – 30Å.
- Ratio \( \frac{d_{\text{pore}}}{d_{\text{molecule}}} \) needs to be in the range 10-20 to be outside configurational diffusion range.
- Catalyst pores need to be in the range of about 100-600Å for free diffusion of molecules in the range 10-30Å.

Importance of Pore Size
Importance of Pore Size

Feed Vaporization and Pre-Cracking:
Bottoms Conversion vs. Mesopore Volume

Kinetic conversion of bottoms increases with 100-600Å pore volume.
Small Pores Increase Coke and Hydrogen

Pilot plant testing, Resid feed 5000 ppm metals/CPS

Coke

<table>
<thead>
<tr>
<th>PV &lt;100 Ang, cc/g</th>
<th>Coke, wt%</th>
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<tr>
<td>0.04</td>
<td>8.2</td>
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<td>0.045</td>
<td>8.4</td>
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<td>0.05</td>
<td>8.6</td>
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<td>0.055</td>
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<td>0.07</td>
<td>9.4</td>
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<tr>
<td>0.075</td>
<td>9.6</td>
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Hydrogen

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<tr>
<th>PV &lt;100 Ang, cc/g</th>
<th>H₂, wt%</th>
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<tr>
<td>0.07</td>
<td>0.07</td>
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<tr>
<td>0.075</td>
<td>0.075</td>
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</tbody>
</table>
Resid Catalysts Require Metals Tolerance

Contaminant Metals

- Sodium
- Iron
- Calcium

Destruction of Exterior Surface Pore Structure

Zeolite Destruction

- Vanadium
- Sodium
- Calcium

Dehydrogenation Catalysts

Nickel
Iron
Vanadium
Reducing Contaminant Coke with Ni Passivation

Davison Ni passivation technologies (e.g., TRM-400 and LCM) lower the amount of reducible nickel.

Ni Passivation Mechanism

\[
\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4
\]

XPS Analysis of Ni on FCC Catalysts

Effect of Matrix Type

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>Counts / Sec</th>
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<tbody>
<tr>
<td>845</td>
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</tr>
<tr>
<td>850</td>
<td></td>
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<td>855</td>
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</tr>
<tr>
<td>865</td>
<td></td>
</tr>
<tr>
<td>870</td>
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NiAl\(_2\)O\(_4\) | Base Ni Trap
NiO | Ni Trap

XPS Data

2000 ppm Ni

Binding Energy (eV)

Counts / Sec

870 865 860 855 850 845
Vanadium Tolerance

**V Traps**
- Reduce coke and hydrogen
- Protect the zeolite from deactivation

“Hot spots” indicate where rare earth (RE) trap interacts with vanadium
Most of the particle remains relatively free of V contamination

The IVT-4 is utilized in IMPACT® technology
Genesis Catalysts for Resid Feeds

- Genesis Catalysts are blends of Midas® with other catalysts.

- For resid feeds, Midas® blended with Impact® provides optimal performance:
  - Excellent coke selectivity
  - Superior bottoms cracking
  - High metals tolerance

- Ratio of Midas to Impact can be adjusted for specific feed and yield objectives.
The GENESIS Catalyst System

- MIDAS is the key component
- Optimize Z/M ratio for each application by blending with high zeolite catalyst
  - IMPACT, Al sol, or Si sol
- Catalyst blend performance often **exceeds** average performance of individual catalysts
- 25 applications world-wide across a broad range of feed types and operating scenarios

**Why does it work?**

- DCR study over 3 feeds with
  - IMPACT
  - MIDAS
  - GENESIS

<table>
<thead>
<tr>
<th>Name</th>
<th>Ni + V</th>
<th>Feed type</th>
<th>Blend Component</th>
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<tbody>
<tr>
<td>Refiner 1</td>
<td>230</td>
<td>VGO</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 2</td>
<td>250</td>
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<td>SPECTRA</td>
</tr>
<tr>
<td>Refiner 3</td>
<td>400</td>
<td>Hydrotreated</td>
<td>ORION</td>
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<tr>
<td>Refiner 4</td>
<td>900</td>
<td>Hydrotreated</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 5</td>
<td>1300</td>
<td>VGO</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 6</td>
<td>1800</td>
<td>VGO</td>
<td>IMPACT</td>
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<tr>
<td>Refiner 7</td>
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<td>VGO</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 8</td>
<td>2000</td>
<td>VGO</td>
<td>AURORA</td>
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<tr>
<td>Refiner 9</td>
<td>2000</td>
<td>Resid</td>
<td>IMPACT</td>
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<tr>
<td>Refiner 10</td>
<td>2500</td>
<td>VGO</td>
<td>ORION</td>
</tr>
<tr>
<td>Refiner 11</td>
<td>2500</td>
<td>VGO</td>
<td>SPECTRA</td>
</tr>
<tr>
<td>Refiner 12</td>
<td>3000</td>
<td>VGO</td>
<td>AURORA</td>
</tr>
<tr>
<td>Refiner 13</td>
<td>3000</td>
<td>Resid</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 14</td>
<td>3000</td>
<td>Resid</td>
<td>AURORA</td>
</tr>
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<td>Refiner 15</td>
<td>3500</td>
<td>Resid</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 16</td>
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<td>Resid</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 17</td>
<td>3800</td>
<td>VGO</td>
<td>IMPACT</td>
</tr>
<tr>
<td>Refiner 18</td>
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<td>Resid</td>
<td>ORION</td>
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<tr>
<td>Refiner 19</td>
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<td>Resid</td>
<td>IMPACT</td>
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<td>IMPACT</td>
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<td>Refiner 25</td>
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<td>Resid</td>
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## Properties of IMPACT and Midas

<table>
<thead>
<tr>
<th></th>
<th>IMPACT</th>
<th>MIDAS</th>
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<tbody>
<tr>
<td><strong>Fresh Properties</strong></td>
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<td></td>
</tr>
<tr>
<td>Al₂O₃ (wt%)</td>
<td>45.2</td>
<td>49.5</td>
</tr>
<tr>
<td>RE₂O₃ (wt%)</td>
<td>4.9</td>
<td>2.0</td>
</tr>
<tr>
<td>SA (m²/g)</td>
<td>317</td>
<td>267</td>
</tr>
<tr>
<td>Zeolite (m²/g)</td>
<td>263</td>
<td>154</td>
</tr>
<tr>
<td>Matrix (m²/g)</td>
<td>54</td>
<td>113</td>
</tr>
<tr>
<td><strong>Deactivated Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA (m²/g)</td>
<td>187</td>
<td>175</td>
</tr>
<tr>
<td>Zeolite (m²/g)</td>
<td>149</td>
<td>92</td>
</tr>
<tr>
<td>Matrix (m²/g)</td>
<td>38</td>
<td>83</td>
</tr>
<tr>
<td>Unit Cell</td>
<td>24.28</td>
<td>24.29</td>
</tr>
<tr>
<td>Hg PSD cm³/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-100 cm³/g</td>
<td>0.338</td>
<td>0.429</td>
</tr>
<tr>
<td>100-1000 cm³/g</td>
<td>0.132</td>
<td>0.279</td>
</tr>
<tr>
<td>1000+ cm³/g</td>
<td>0.172</td>
<td>0.049</td>
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</table>
GENESIS catalysts demonstrate a **superior coke to bottoms relationship** that either component alone, regardless of the feed quality!
Commercial Example of GENESIS Synergy (Resid Feed)
Conclusions

- FCC Resid cracking is usually economic despite difficulties because of extremely low value of Resid.

- Difficulties for cracking Resid relate to impurities (CCR, metals, N) and the resulting high $\Delta$ Coke.

- Resid Catalysts must be designed for improved coke selectivity, bottoms cracking, metals tolerance and stability.
  - Zeolite UCS should equilibrate in the desired range of 24.28 - 24.34 Å.
  - ZSA/MSA should be adjustable – for more resid, increase MSA.
  - Pore volume in the 100-600Å range should be high,
  - Catalysts should contain both Ni and V traps.
  - Genesis grades (blends of Midas and Impact) have all these features.