Population Balance Modeling: A Useful Approach for Understanding FCC Particulate Attrition

Jennifer Wade, David Stockwell and Robert Andrews - BASF
S. B. Reddy Karri, Yeook Arrington, and Ray Cocca – PSRI
Galveston, TX       May 3-6, 2011

BASF Investment in FCC Catalyst Technology Innovation

- Continued commitment to innovation through investment in R&D
- BASF Operating 5 FCC Technology Development Platforms:
  - FCC emissions reductions – PM / NOx / SOx
  - Incremental demand for diesel over gasoline
  - Next generation high conversion - post Distributed Matrix Structure (DMS)
  - Heavier crudes to refineries
  - Growing petrochemicals demand – particularly propylene

Controlling Particulates is More Important Than Ever

- Tightening PM regulations
- Standards for reconstructed FCCUs
  - < 1 lb / 1000 lb coke burned or < 0.04 grains / dry scf
- National Ambient Air Quality Standard (40 CFR part 50)
  - PM2.5 ≤ 35 mg / m³ per 24 hour average
  - For areas in non-attainment, SIPs are due 12/2012
  - target stationary sources

Avoid operational problems
-Opacity constraints
- Expander blade vibrations
- Cyclone dipleg deposits
- Air grid plugging
- Waste heat boiler fouling
- Fuel oil quality specifications
Tackling the Attrition Problem

- Industry demands a more attrition proof FCC catalyst without sacrificing performance or yield structure
- In order to successfully design such a catalyst, need to first understand how catalyst particles attrit in commercial units
- Identify the best lab method that accurately predicts catalyst attrition to best mimic commercial forces
- Identify which catalyst properties lead to reduced attrition to drive future catalyst technology developments

Catalyst Attrition Mechanisms

- Particles can Fracture or Abrade
  - Fragments vs. micro-fines generation
  - Dependent on catalyst properties and unit forces (cyclone loadings, superficial velocities, wall collisions, gas jet impingement, etc.)
- Population Balance Model (PBM)
  - Measures particle breakage rate and probability to break into fragments versus fines as a function of particle size and time
  - Elucidates the dominating attrition mechanism

What is Population Balance Modeling?

- Predicts the degradation rate of particles of a given size to smaller sizes ($S_j$)
- Predicts the probability at which particles are formed from larger size bins ($R_j$)

Characterize Catalyst Size Distributions

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Product Name</th>
<th>Breakage</th>
<th>Abrasion</th>
<th>SPT</th>
<th>SFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Fractured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50-100</td>
<td>Fractured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-50</td>
<td>Fractured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-25</td>
<td>Fractured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-10</td>
<td>Fractured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>Fractured</td>
<td></td>
<td></td>
<td>SPT</td>
<td></td>
</tr>
</tbody>
</table>

* SPT = small particle transitions
Catalyst Attrition Mechanisms

- Fracture, b<sub>2.3</sub>
- Fracture, b<sub>2.4</sub>
- Abrasion, b<sub>3.5</sub>
- Abrasion, b<sub>4.6</sub>

PBM Size Dependent Material Balance

Generation of size i from larger size j:

\[ \Delta t \left( w_i(t + \Delta t) - w_i(t) \right) = \sum_{j=1}^{i-1} h_{ij} S_{m_j} \]

Rate of size i lost: slurry, PM controls and stack

\[ w_{\text{loss}} = w_i \]

Rate of size i removed from e-cat

\[ w_{\text{cat-e}} = m_i \]

FCCU Data Collection

Complete Catalyst Material Balance

- Need complete material balance and PSD of each catalyst stream.
- Assumption that unit is under steady state.
• 27-68% of total catalyst addition is lost to the slurry or out the flue gas train.

• Reducing losses allows a refiner to lower catalyst addition rates.

• Net Attrition is a rough measure to assess how much of the cat losses are due to attrition.

\[ \sum PBM = \text{Breaking and formation rates as a function of particle size} \]

• All -20 is formed through attrition and particles leave the unit in under a day.

• PBM allows for more accurate accounting of the size dependent Mean Residence Time.

\[ MRT = \frac{\text{Fresh cat}}{\text{PBM}} \]

• Abrasion is most important in 5 out of 6 FCCUs.

• Total attrition accounts for all attrition transitions, even those that occur through several size bins.

• Refinery A shows fracture and abrasion to both be important. This unit also shows the highest total attrition.
Population Balance Model Can Be Applied to FCCUs and Laboratory Attrition Tests

Laboratory Attrition Tests Seek to Predict Refinery Performance

- Many configurations, but same goal: degrade catalyst through collisions with walls, catalyst particles or other media
- Jets of air are most often the driving force
- Result is a quantity of fines particles generated for a designated test duration
- Different attrition tests can lead to inconsistent catalyst rankings

Attrition Apparatus

Lowest attrition catalyst in test B looks the worst in test A!
Air Jet loss rates

- Test run with e-cat from Refinery D
- Tests are run until 25 - 50% of fresh catalyst is degraded to fines, matching commercial loss rates
- Initial, transient loss followed by a steady state loss rate
- Single parameter index will not capture all of the attrition properties

Attrition Test Material Balance

\[
\frac{d}{dt}m_i(t) = \sum_{j<i} \left( b_{ij} S_j(t) + b_{ij} S_{ij}(t) \right) + \sum_{j<i} \left( b_{ij} S_{ij}(t) \right) - W_i \cdot M_i \cdot \text{rate of attrition, g/h}
\]

Air Jet and Roller PBM Results
Behavior at two velocities is very different.
- Steady state loss rate achieved at 150 fps
- Long transient with a drop to very low attrition rates at 600 fps

Test methods vary in predominance of Fracture vs Abrasion
- Air jet is 27% fracture → in line with commercial results
- Conical jet cup is predominately abrasion
  - At high velocities attrition is highly transient and approaches zero
  - Low velocity measurements can be impractical
- Roller is 59% fracture

Single value attrition index is not sufficient: transient loss, the lifetime of the transient loss and the steady state attrition rate

Identification of a representative test method helps guide future attrition resistant catalyst development and allows refineries to accurately assess differences in catalyst attrition tendency
BASF Offers Low Microfines (LMF) Technology

- Low microfines (LMF) technology can be applied to most FCC products with little change to yield patterns or selectivity
- LMF catalyst exhibit fewer attrition products by both particle fracture and abrasion
- 20-60% relative emission reductions are possible
- Typical air jet attrition rates:
  - Standard Catalyst (e.g. NaphthaMax®) = 4 wt%/hr
  - LMF Grade < 2 wt%/hr
- BASF will provide a prediction for each case to determine the suitability of the catalyst to the application

LMF Application

- Commercial unit wanted to reduce opacity
  - Compared NaphthaMax® to NaphthaMax® LMF
- FCC was of standard geometry with typical hardware
  - UOP SBS, advanced feed injection and riser termination with a TSS
- Unit experience was positive
  - No yield degradation
  - Lowered opacity at similar operation

Opacity Reduction with NaphthaMax® LMF

- Graph comparing opacity reduction with NaphthaMax® and NaphthaMax® LMF
Clear Shift in Particle Sizes Leaving the Regenerator

- Stack surveys conducted routinely
- Measurement taken at constant solids
- Dramatic reduction in small particles
  - 87 → 43% < 2.5 μm

Summary

- Population Balance Model enables the understanding of catalyst attrition mechanisms
- Early results show abrasion based attrition in commercial units is most important
  - Air Jet best reflects 5 out of 6 commercial units
  - This may not be true in all cases, may need more than one test
- BASF LMF technology lowers microfines without impacting yield performance
- A clear metric to gauge catalyst attrition will aid in the development of future LMF technologies

Acknowledgements

Key External Contributors
- Kerry Johanson, Material Flow Solutions, Gainesville, Florida, USA
- C. J. Farley, Astron International, Houston, Texas, USA

Author Contact Information
- jennifer.wade@basf.com
- david.stockwell@basf.com
- robert.andrews@basf.com
- reddy.karri@psrichicago.com
- yeook.arrington@psrichicago.com
- ray.cocco@psrichicago.com
NaphthaMax is a trademark of BASF.

Although all statements and information in this publication are believed to be accurate and reliable, they are presented gratis and for guidance only, and risks and liability for results obtained by use of the products or application of the suggestions described are assumed by the user. NO WARRANTIES OF ANY KIND, EITHER EXPRESS OR IMPLIED, INCLUDING WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, ARE MADE REGARDING PRODUCTS DESCRIBED OR DESIGNS, DATA OR INFORMATION SET FORTH. Statements or suggestions concerning possible use of the products are made without representation or warranty that any such use is free of patent infringement and are not recommendations to infringe any patent. The user should not assume that toxicity data and safety measures are indicated or that other measures may not be required.

© 2010 BASF