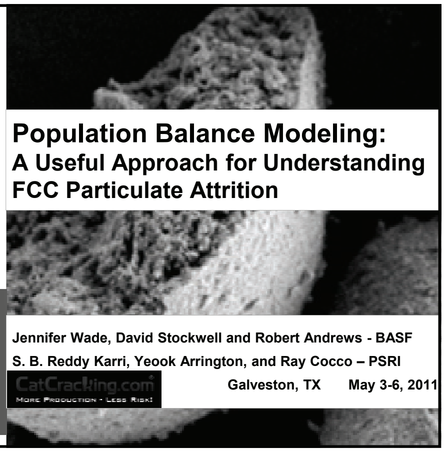

Population Balance Modeling:
A Useful Approach for Understanding FCC Particulate Attrition

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S. B. Reddy Karri, Yeook Arrington, and Ray Cocco – PSRI

CatCracking.com More Production - Less Risk!
Galveston, TX May 3-6, 2011

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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 / NO_x / SO_x**
  - 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

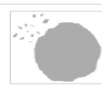
- **Tightening PM regulations**
- **Standards for reconstructed FCCUs**
  - **< 1 lb / 1000 lb coke burned or < 0.04 grains / dry scf**
- **National Ambient Air Quality Standard (40 CFR part 50)**
  - **PM2.5 ≤ 35 mg / m^3 per 24 hour average**
    - **For areas in non-attainment, SIPs are due 12/2012**
    - **target stationary sources**

Avoid operational problems	
▪ Opacity constraints	▪ Air grid plugging
▪ Expander blade vibrations	▪ Waste heat boiler fouling
▪ Cyclone dipleg deposits	▪ 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?

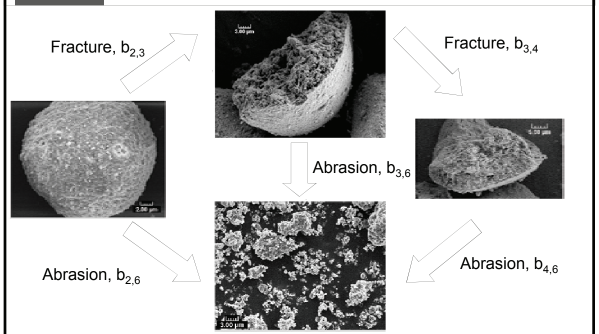
- **Predicts the degradation rate of particles of a given size to smaller sizes (S_i)**
- **Predicts the probability at which particles are formed from larger size bins ($b_{i,j}$)**

Characterize Catalyst Size Distributions

Starting Size, microns		Product Size, microns					
		> 150	80-150	40-80	20-40	10-20	0-10
1	> 150		Fracture				
2	80-150			Fracture		Abrasion	
3	40-80				Fracture		
4	20-40		Forbidden			SPT	
5	10-20						SPT
6	0-10						

* SPT = small particle transitions

Catalyst Attrition Mechanisms



PBM Size Dependent Material Balance

Generation of size i from larger size j.

$$+\sum_{j=1}^{i-1} b_{i,j} S_j m_j$$

Fresh Cat additions of size *i*

$$+\frac{w_{fresh} * m_{i,fresh}}{\Delta t}$$

Rate of change of size *i* in a fluid bed

$$\frac{w_i(t+\Delta t)-w_i(t)}{\Delta t}$$

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

$$-\frac{w_{losses} * m_{i,losses}}{\Delta t}$$

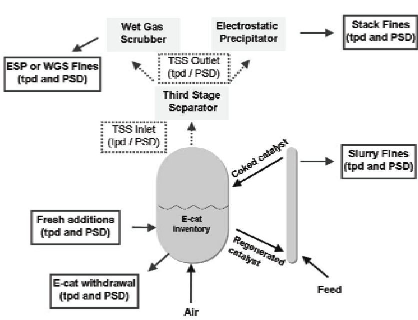
Rate of size i removed from e-cat

$$-\frac{w_{e-cat} * m_{i,e-cat}}{\Delta t}$$

Rate size *i* destroyed by attrition

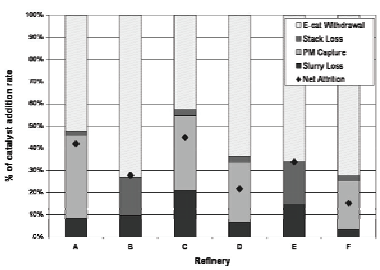
$$-S_i m_i$$

FCCU Data Collection
Complete Catalyst Material Balance



- **Need complete material balance and PSD of each catalyst stream.**
- **Assumption that unit is under steady state.**

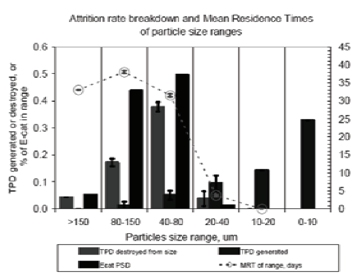
Catalyst Losses in Six FCCUs



- 27-58% 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.

$$\frac{\sum_{i=1}^{6} \left| m_{i\_ecat} + m_{i\_losses} - m_{i\_fresh} \right|}{2}$$

Applying the Population Balance Model



- PBM determines 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**

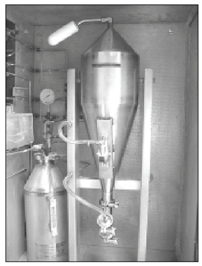
$$MRT_i = \frac{w_i}{Fresh_i\_tpd + \sum_{j=1}^{i-1} b_{i,j} S_j m_j}$$

Attrition Properties of 6 FCCUs

Refinery	A	B	C	D	E	F
total attrition / cat adds	84%	36%	60%	25%	43%	16%
wt% Fracture	43 ± 13%	30 ± 9%	32 ± 9%	27 ± 7%	21 ± 5%	13 ± 5%
wt% Abrasion	**53 ± 14%**	**64 ± 13%**	**65 ± 11%**	**71 ± 8%**	**75 ± 7%**	**86 ± 5%**
wt% SPT	4 ± 2%	6 ± 4%	3 ± 2%	2 ± 1%	4 ± 2%	1 ± 1%

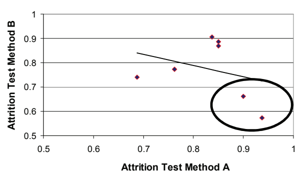
- ***Abrasion* is most important in 5 out of 6 FCCUs**
- **Total attrition accounts for all attrition transitions, even those that occur through several size bins**
- **Refinery A shows fracture and abrasion to both be important. This unit also shows the highest total attrition**

Population Balance Model Can Be Applied to FCCUs and Laboratory Attrition Tests



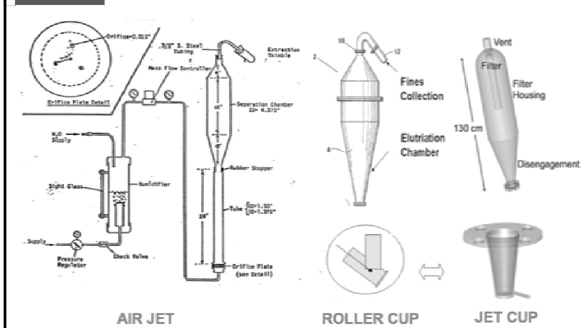
Laboratory Attrition Tests Seek to Predict Refinery Performance

- 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



Lowest attrition catalyst in test B looks the worst in test A!

Attrition Apparatus



Air Jet loss rates

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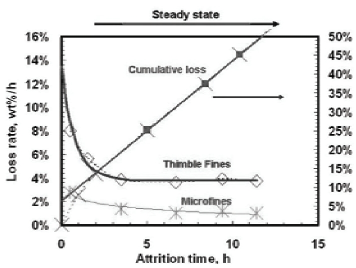

- Test run with e-cat from Refinery D
- Tests are run until 25 - 50% of fresh catalyst is degraded to fines, matching commercial loss rates
- Initial, transient loss followed by a steady state loss rate
- Single parameter index will not capture all of the attrition properties

Attrition Test Material Balance

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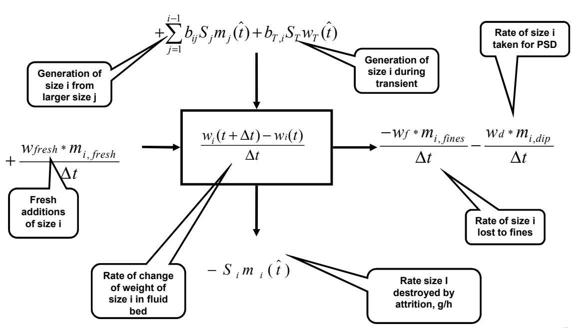

Air Jet and Roller PBM Results

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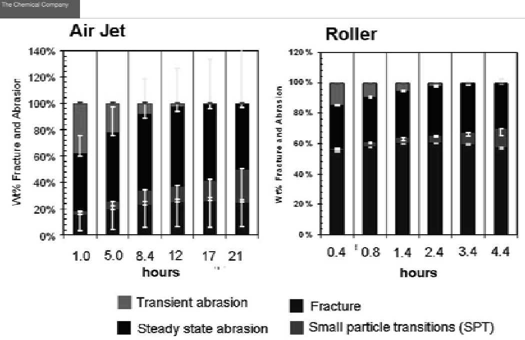

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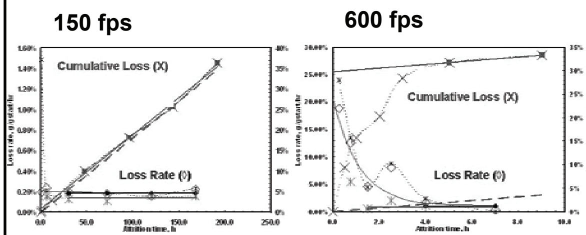
PSRI Conical Jet Cup loss rates



- **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

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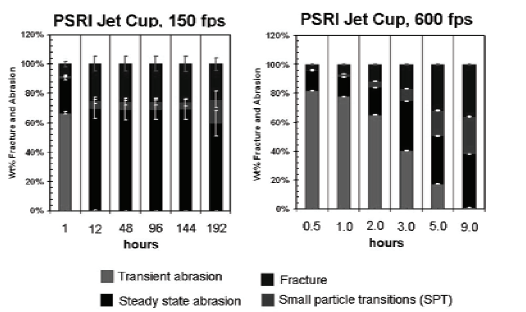
PSRI Conical Jet Cup



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Lab Attrition Test Summary

- **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 asses differences in catalyst attrition tendency**

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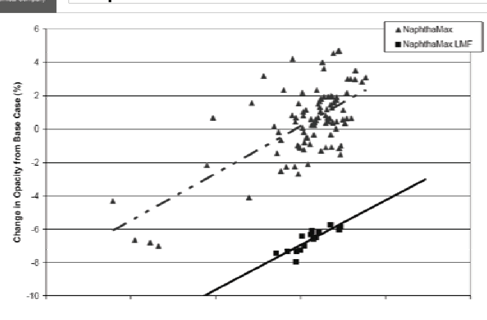
BASF Offers Low Microfines (LMF) Technology

- 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

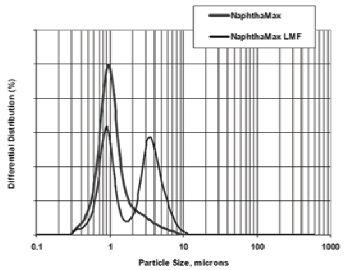
- Commercial unit wanted to reduce opacity
  - Compared NaphthaMax® to NaphthaMax® LMF
- FCC was of standard geometry with typical hardware
  - UOP SBS, advanced feed injection and riser termination with a TSS
- Unit experience was positive
  - No yield degradation
  - Lowered opacity at similar operation

Opacity Reduction with NaphthaMax® LMF



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

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