Cat Cracker Seminar
August 19-20, 2014
Royal Sonesta Hotel
Houston, TX

CAT-14-102  Evaluating Equilibrium Catalyst (Ecat) Data

Presented By:

Bob Riley
Senior Technical Sales Manager
Grace Catalysts Technologies
Temecula, CA
This paper has been reproduced for the author or authors as a courtesy by the American Fuel & Petrochemical Manufacturers. Publication of this paper does not signify that the contents necessarily reflect the opinions of the AFPM, its officers, directors, members, or staff. Requests for authorization to quote or use the contents should be addressed directly to the author(s)
Sample Shipment Safety

Ecat sample shipment is a routine activity, but there are multiple examples of receipt of dangerously packaged shipments.

Work with your catalyst vendors to understand recommended shipment packaging and safety instructions.
Objectives

Brief review of Ecat properties
Demonstrate different ways to view catalyst data
Review specific case studies
Active participation
What are the Key Features of FCC catalyst?

- Optimized SURFACE AREA
- Tailored PORE SIZE DISTRIBUTION
- Tailored ACIDITY
- Proper PARTICLE SIZE DISTRIBUTION
- Other Physical Properties

ACTIVITY & SELECTIVITIES

FLUIDIZATION & RETENTION
What Types of Tests are Run on Ecat Samples?

Activity/Selectivity Tests

- MAT or ACE cracking at standard conditions
- Determines Activity and Selectivities

Parameters to track from these tests

- Activity
- Gas Factor
- H₂ Yield
- Coke Factor
- Single point ACE yields
What Types of Tests are Run on Ecat Samples?

**Chemical Composition Tests**

- XRF or ICP testing for complete chemical analysis
- Carbon analysis
- Determines contaminant metals profile
- Often useful for tracking catalyst turnover

**Parameters to track from these tests**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content</td>
<td>MgO</td>
</tr>
<tr>
<td>Ni</td>
<td>P2O5</td>
</tr>
<tr>
<td>V</td>
<td>Sb</td>
</tr>
<tr>
<td>Na</td>
<td>All Trace Chemical Contaminants (CaO, K2O, Pb, etc.)</td>
</tr>
<tr>
<td>Re2O3</td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td></td>
</tr>
</tbody>
</table>
What Types of Tests are Run on Ecat Samples?

Physical Property Tests

- Surface area
- Apparent bulk density (ABD)
- Pore volume
- Particle size distribution
- Umb/Umf
- Others

Parameters to track from these tests

- Surface areas: total, zeolite, and matrix
- Unit Cell Size
- ABD and pore volume
  - 0-40, 40-80, and >105 micron fraction (particle size)
  - $U_{mb}/U_{mf}$
Ecat Activity

Defined as Conversion (100 – LCO (wt%) – Slurry (wt%)) as measured in a microscale test unit (fixed cat to oil).

Kinetic Conversion = \[
\frac{\text{Conv}}{100 - \text{Conv}}
\]

Tested after carbon is burned off catalyst

85% of North American FCC’s are represented in the distribution
Factors that Impact Activity

Fresh catalyst additions

Metals contamination
- Vanadium
- Alkali metals (Na, K)
- Alkaline earths (Ca)

Catalyst reformulation
- Activity per unit of surface area
- Incorporation of a vanadium trap
- Zeolite input

Unit severity
- Mode of operation (Full vs. Partial)
- Thermal/Hydrothermal deactivation

Re2O3 or other stabilization compounds
Activity Recovers Quicker than Bulk Properties
Activity Testing - Selectivities

Gas factor (GF)
- Molar hydrogen-to-methane ratio from the ACE unit

Hydrogen yield (H2 Yield)
- Hydrogen yield measured in SCFB from the ACE unit

Coke factor (CF)
- Ratio of the ACE coke yield (wt%) to the kinetic activity

Factors that impact GF, H2 Yield, and CF
- Catalyst formulation & design
- Contaminant metals (Ni, V, Cu, Fe, etc.)
- Metals tolerance of the fresh catalyst
- Antimony (Sb) injection

Full yield profiles can also be tracked via Ecat ACE testing
Contaminant Impacts on FCC Catalysts

**Zeolite Dealumination / Zeolite Destruction**
- Vanadium
- Sodium
- Calcium
- Potassium

**Destruction of Exterior Surface / Pore Structure**
- Sodium
- Iron
- Calcium

**Dehydrogenation Catalysts**
- Nickel
- Iron
- Vanadium
- Molybdenum
- Copper

**Common Sources of Metals**
- Organic Complexes in Crude Oils
- Additives in Crude extraction
- Entrained metals from other catalytic processes
- Tramp metals (Iron)
- Non-Desalted Crude (Sea Water)
- Lube Extracts
- Purchased Ecat
- Micro-sized mineral particulates in feed (often seen in Shale Oil)
Dealumination of Zeolite / Zeolite Destruction

Vanadium
- Deactivates by destroying zeolite surface area and reducing activity
- Forms vanadic acid in the regenerator (H₃VO₄)
- Rule of Thumb: 500 ppm (V + Na) lower catalyst activity by ~ 1 number
- Range: 70 – 7800 ppm (includes SOx reducing additive V)
- Average: 1974 ppm (includes SOx reducing additive V)
- More severe activity loss in full burn units (more oxidizing environment in regenerator)

Alkali metals and alkaline earths
- Form eutectics with elements in fluid cracking catalyst which can fuse at regenerator conditions, causing negative yield impacts
- Harmful effects are magnified when regenerator severity is increased

Sodium (Na), wt%
- Range: 0.09 – 1.42 wt%
- Average: 0.27 wt%

Calcium (CaO), wt%
- Range: 0.02 – 2.28 wt%
- Average: 0.15 wt%

Potassium (K₂O), wt%
- Range: 0.02 – 0.37 wt%
- Average: 0.07 wt%
Each FCCU Responds Uniquely to Contamination

The graph shows the relationship between Activity, wt% and V + Na, ppm with slopes indicated as follows:

- Black dots: Slope = -2.9 (per 1000 ppm V+Na)
- Red squares: Slope = -2.6 (per 1000 ppm V+Na)
- Blue diamonds: Slope = -7.4 (per 1000 ppm V+Na)
Each FCCU Responds Uniquely to Contamination
Example: Na Impact on Catalyst Activity
Usefulness of Ecat and Fines Analysis

Waste heat boiler leak
Potassium Contamination

Process recycle ASO (Acid Soluble Oil) which contains KOH
Destruction of Exterior Surface/Pore Structure

**Ecat Iron (Fe) = Fresh Catalyst Fe + Added Fe**

- Fe is naturally present in the clay used to manufacture catalyst, but this Fe does not negatively impact unit performance
  - Fe in clay may vary with catalyst supplier and formulation
- From secondary crude recovery processes and more recently in Tight Oils
- Coats catalyst surface – can cause severe conversion loss by blocking access to sites
- Fe acts as reverse SOx reducing additive
  - Fe reacts with H2S in the riser to form FeS, which in the regenerator is oxidized and eventually released as SOx
- Watch for a drop in ABD
  - Range: 0.23 – 1.47 wt%
  - Average: 0.52 wt%

**Calcium (CaO)**

- Frequently found with Fe in Tight Oils
- Forms a eutectic with Fe and alumina that can fuse and form nodules on the catalyst particles
Case Study: Troubleshooting Conversion Loss

Graph 1: Conversion vs. Time Scale

Graph 2: Slurry API vs. Time Scale
Case Study: Troubleshooting Conversion Loss
Case Study: Troubleshooting Conversion Loss

![Graphs showing CaO and MgO content over time](image-url)
Troubleshooting Conversion Loss – SEM

Added Fe = 0.36 wt%
CaO = 0.18 wt%
Serious poisoning evident

Added Fe = 0.15 wt%
CaO = 0.1 wt%
No Evidence of Fe Nodules
Troubleshooting Conversion Loss – EPMA

Fe
- 0.15 wt% Added
- 0.32 wt% Added
- 0.36 wt% Added

Ca
- 0.1 wt%
- 0.18 wt%
- 0.18 wt%

Lower apparent intensity due to larger scale
Dehydrogenation Catalysts

**Nickel (Ni) / Copper (Cu)**
- Strong dehydrogenation catalyst
- Significant increase in coke and gas
- Does not cause catalyst activity to decline for most units
- Nickel passivators such as Sb are used when high nickel content feeds are charged to the unit

**Nickel (Ni), ppm**
- Range: 26 – 16,372 ppm
- Average: 1,587 ppm

**Copper (Cu), ppm**
- Range: 7 – 400 ppm
- Average: 38 ppm

**Molybdenum (Mo), ppm**
- Present in some hydrotreated oils
- Very strong dehydrogenation agent
- May slowly climb as hydrotreaters near end of run, or spike if contaminated feed is purchased

**Vanadium, ppm**
- Acts at about ¼ the dehydrogenation effect of Ni
Case Study: Nickel Trap

![Graph showing Gas Factor vs Nickel Equivalent]

- Catalyst 1
- Catalyst 2 (Nickel Trap)
Antimony Passivates Ni

- ~0.30 ppm Sb/ppm Ni
- ~1000 ppm Ni
Carbon on regenerated catalyst (CRC)

- Measured on the Ecat to determine the efficiency of the regenerator
- Full combustion units typically operate below 0.15 wt%
- Partial burn units typically operating 0.1-0.4 wt%
- Range: 0.01 – 1.2 wt%
- Average: 0.11 wt%

Factors that impact carbon

- Regenerator temperature
- Regenerator design
- Mode of operation (Full vs. Partial)
- Air distribution
- Low excess O₂
- Residence time
Case Study: High CRC

![Graph showing Ecat Carbon wt% over time scale](image)
Particle Size Distribution

Ecat 0-40µ
- Used to determine cyclone efficiency and to identify attrition sources
- Range: 0 - 20µ wt%
- Average: 4µ wt%

Ecat 40-80µ
- Most important fraction for catalyst fluidization
- Range: 24 - 57µ wt%
- Average: 44µ wt%

Ecat APS, µm
- Used to determine cyclone efficiency and track both retention and fluidization properties
- Range: 67 – 109 µm
- Average: 81.8 µm

Factors that impact Particle Size Distribution
- Unit catalyst retention (cyclone performance)
- 0-40µ on fresh catalyst
- Attrition sources
- Fresh cat add rates
- Purchased Ecat adds & quality
- Fresh catalyst attrition mechanism
Case Study: Catalyst Retention

FCCU background

- Gas Oil service
- Typical catalyst additions: 3 TPD

Problem: Catalyst Loss

- Adding 5-7 TPD to maintain regenerator bed level
Case Study: Catalyst Retention

![Graph of catalyst particle size distribution showing decline in catalyst retention](Image)

**Unit Shutdown**
Case Study: Catalyst Retention

<table>
<thead>
<tr>
<th>UOM</th>
<th>APS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>μm</td>
</tr>
<tr>
<td>Increased Losses</td>
<td>μm</td>
</tr>
</tbody>
</table>
Case Study: Catalyst Retention

![Graph showing wet gas scrubber purge water example: decline in catalyst retention.](image)
Case Study: Catalyst Retention

Found regenerator secondary cyclone diplegs plugged

Unit Shutdown
Case Study: Catalyst Retention

![Diagram of Ecate Particle Size Distribution](image)
Fluidization

Umb/Umf (fluidization factor)
- Calculated number used to determine the fluidization capabilities of an Ecat
- Higher values represent an inventory with better flow characteristics.
- The value of a “good” Umb/Umf is unit dependent
- Number is valuable to units that struggle with catalyst circulation issues

Factors that impact Umb/Umf
- 0-45
- APS

\[
\frac{U_{mb}}{U_{mf}} = \frac{2300 \times \mu_g^{0.126} \times \mu^{0.523} \times e^{0.716F}}{D_p^{0.8} \times g^{0.934} \times (\rho_p - \rho_g)^{0.934}}
\]

- U_{mb} = Minimum Bubbling Velocity, m/s
- U_{mf} = Minimum Fluidization Velocity, m/s
- F = 0-45 μm Fraction in Catalyst
- μ_g = Gas viscosity, kg/ms
- D_p = Mean Particle Diameter = m
- ρ_p, g = Particle and Gas Properties, kg/m³
- g = Gravitational Constant = 9.8 m/s²
Case Study: Catalyst Retention
Case Study: Catalyst Retention

![Graph showing Ecat UMB/UMF with a decline in catalyst retention example]
Tracking Additive Performance – Ecat vs. Fines

SOx reducing additive effect:
- MgO
- Vanadium
- Re$_2$O$_3$

NOx reducing additives can effect:
- Cu
- Re$_2$O$_3$

ZSM5 additive effect:
- P$_2$O$_5$
  - Increases in C3 and C4 olefins and gasoline octane at the expense of cat gasoline
  - Increases volume gain

CO Promoter:
- Noble metal based – not typically measurable in Ecat
- May make NO$_x$ if used in high concentrations
Usefulness of Ecat and Fines Analysis

Ecat MgO and Fines MgO

MgO, ppm

Time Scale

Additive Change

CAT-14-102  Page 40  2014 Cat Cracker Seminar
Conclusion

Ecat, fines, and fresh catalyst analysis are pieces of the puzzle that can be used in troubleshooting FCCU problems.