FCC Unit Evaluation Practices

Alan Sweezey, Executive Account Manager
FCC Unit Evaluation Practices

Overview:

- Refinery FCC Unit Monitoring Practices
- Industry Catalyst Selection Methodology
- Laboratory Catalyst Evaluation Techniques
  - Deactivation
  - Testing
  - Data Evaluation / Scale-Up

July 12, 2012
Regular FCC Unit Monitoring Practices

- Determine and document actual Unit Operation / Results
  - Routine Mass Balances
  - Test Runs
- Compare Feedstock Quality with Baseline
- Compare Actual Operation with Unit Limits
Determine Actual FCC Unit Results
Routine Balances are Critical

Regular Unit Monitoring Has Two Parts:

1. Unit Mass Balances
   Determine flow rates for feedstock and products
   Determine densities / compositions of streams
   Typically calculated daily or weekly

2. Unit Test Runs (or Base Case)
   Involves close monitoring of unit for set period of time (>24 hr)
   Requires additional resources for operations and laboratory analyses
   Conducted as needed for more exact evaluation of unit operation and product yields – at least once per year
Regular (Daily/Weekly) FCC Unit Mass Balance Procedures

- **Most Basic Effort Provides**
  - Rough material balance (at plant cut points, etc.)
  - Non-normalized product yields
  - Mass closure target +/- 2%

- **Recommended Balance Provides**
  - Flows corrected for temperature, density, cut points, composition
  - Heat balance & catalyst circulation
  - Detailed feedstock quality evaluation

- **Review trends for evaluation & operating adjustments**
Planned Unit Test Runs = The “Gold Standard” of FCC Evaluation

- Stable unit operation over a day with consistent feedstock quality & without side streams
- Complete Feedstock Analysis
- Complete heat balance & catalyst circulation
- Normalized product yields “as produced”
- Product yields at standard cut points / components

This level of evaluation is required to begin a unit or catalyst evaluation or to review catalyst changes
## Base Case Test Runs – Example of Results

### FCC-SIM SUMMARY

<table>
<thead>
<tr>
<th>Net Profit</th>
<th>462861 $/day</th>
<th>S/day</th>
<th>3</th>
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<tr>
<td>Unit Profit</td>
<td>18.5144 $/bbl</td>
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<tr>
<td>Case Num</td>
<td>3</td>
<td></td>
<td></td>
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<tr>
<td>Run Time</td>
<td>39763.3 LMT</td>
<td>39763.3 LMT</td>
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### PRODUCT YIELDS

<table>
<thead>
<tr>
<th>wt % FF</th>
<th>vol % FF</th>
<th>lb/hr</th>
<th>bbl/d</th>
<th>FOE, vol % PRICES</th>
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<tr>
<td>Hydrogen</td>
<td>0.0325</td>
<td>107.931</td>
<td>0.1841</td>
<td>4.41 $/MMBtu</td>
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<td>Hydrogen Sulfide</td>
<td>0.7938</td>
<td>268.311</td>
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<td>Methane</td>
<td>0.1259</td>
<td>418.144</td>
<td>2.9792</td>
<td>4.41 $/MMBtu</td>
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<td>Ethane</td>
<td>1.1799</td>
<td>392.119</td>
<td>2.6502</td>
<td>4.41 $/MMBtu</td>
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<td>Ethylene</td>
<td>0.9974</td>
<td>331.477</td>
<td>2.2249</td>
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<td>Propane</td>
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<td>3.4958</td>
<td>645.99</td>
<td>87.344</td>
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<td>Propylene</td>
<td>4.369</td>
<td>7.642</td>
<td>145.198</td>
<td>191.05</td>
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<td>N-Butane</td>
<td>0.7182</td>
<td>1.1216</td>
<td>2386.86</td>
<td>280.395</td>
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<tr>
<td>Isobutane</td>
<td>4.8239</td>
<td>7.8202</td>
<td>1603.15</td>
<td>1955.06</td>
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<td>1-Butene</td>
<td>0.5544</td>
<td>0.8414</td>
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<td>C-2-Butene</td>
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<td>1,3-Butadiene</td>
<td>0.0453</td>
<td>0.0659</td>
<td>150.687</td>
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<td>Light Naphtha</td>
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<td>----</td>
<td>----</td>
<td>----</td>
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<td>Medium Naphtha</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<td>Total Naphtha</td>
<td>49.892</td>
<td>61.1501</td>
<td>165829</td>
<td>1910.5</td>
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<td>Light LCO</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<tr>
<td>Heavy LCO</td>
<td>----</td>
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<td>----</td>
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<tr>
<td>Light Cycle Oil</td>
<td>13.3574</td>
<td>12.7531</td>
<td>44391.3</td>
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<td>Heavy Cycle Oil</td>
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<tr>
<td>Clarified Oil</td>
<td>11.5724</td>
<td>10.0683</td>
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<td>Coke</td>
<td>6.3806</td>
<td>21204.8</td>
<td>68.4 $/lb</td>
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<td>Total Products</td>
<td>100</td>
<td>108.053</td>
<td>332335</td>
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<tr>
<td>HEAT OF CRACKING</td>
<td>196.965 Btu/lb</td>
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### FRESH FEEDS

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<tr>
<th>Cost</th>
<th>$/bbl</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>HTR Btm TOTAL</th>
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<tbody>
<tr>
<td>Name</td>
<td>----</td>
<td>Feed 1</td>
<td>Feed 2</td>
<td>Feed 3</td>
<td>FEED 4</td>
<td>FEED 5</td>
<td>HTR Btm FCC BLEND</td>
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<tr>
<td>Total Rate</td>
<td>bbl/d</td>
<td>25000</td>
<td>VGO</td>
<td>25000</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Gravity</td>
<td>°API</td>
<td>23.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>TBP 10% Point</td>
<td>°F</td>
<td>600.957</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>TBP 50% Point</td>
<td>°F</td>
<td>810</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>TBP 90% Point</td>
<td>°F</td>
<td>966</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Sulfur</td>
<td>wt %</td>
<td>1.92</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Basic Nitrogen</td>
<td>wt %</td>
<td>0.0619</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

### RISERS

| Feed Rate | bbl/d | 1 | 2 | 25000 | ---- |
| Feed Temperature | °F | 1321.62 | ---- | ---- |
| Inlet Mix Tempera | °F | 1348.39 | ---- | ---- |
| Outlet Temperatu | °F | 1321.62 | ---- | ---- |
| Cat/Oil Ratio | wt/wt | 6.3806 | 1288.96 | 0.024 |
| CCR | ton/min | 18.9938 | ---- | ---- |
| Steam Rate | lb/hr | 700 | ---- | ---- |
| Lift Gas | MSCFH | 0 | ---- | ---- |
| HC Vaporization | wt % | 100 | ---- | ---- |
| Residence Time | seconds | 5.6761 | ---- | ---- |
| Inlet Velocity | ft/s | 11.7632 | ---- | ---- |
| Heat of Cracking | Btu/lb | 196.965 | ---- | ---- |

### REGENERATORS

| Bed Temperature | °F | 1321.62 | ---- | ---- |
| Flue Gas Temperature | °F | 1348.39 | ---- | ---- |
| Flue Gas CO2 vol % | 15.6615 | ---- | ---- |
| Flue Gas CO vol % | 1.3895 | ---- | ---- |
| Flue Gas O2 vol % | 1.4996 | ---- | ---- |
| Total Air Rate | MSCFH | 3774.34 | ---- | ---- |
| CRC | wt % | 0.024 | ---- | ---- |
| Bed Cooling | MMBtu/h | 0 | ---- | ---- |
| Flue Gas Flow Rate/lb/hr | 306.81 | ---- | ---- |
| Superficial Velocity | ft/s | 1.6415 | ---- | ---- |

### CATALYST

| Activity | Mat % | 80 | ---- | 77 |
| Surface Area | m2/g | 275 | 136.145 | ---- |
| Nickel | ppmw | 0 | 128.669 | ---- |
| Vanadium | ppmw | 0 | 722.016 | ---- |
| Sodium | ppmw | 0 | 0 | ---- |
| Make-up Rate | t/d | 10.8806 | ---- | ---- |
| ZSM 5 Content | wt % | 0 | ---- | ---- |
| Zeolite Content | wt % | ---- | ---- | ---- |
| Rare Earth Content | wt % | ---- | ---- | ---- |
| Alumina Content | wt % | ---- | ---- | ---- |

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**BASF**

The Chemical Company

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**July 12, 2012**
Using Mass Balance / Test Run Results

- Compare actual product yields, & results vs. targets
- Determine the actual unit temperatures/flows compared to process limits (regenerator temperature, catalyst circulation, wet gas compressor flow, air flow, etc.
- Model feedstock quality to determine effects on performance
- Document Test Run Results
- Adjust operating variables, catalyst / additive addition to optimize results within process limits
Potential Test Run Problems

- Time and resources – unit engineer with experience
- Preliminary unit balance not done
- Flow instruments not “zeroed” / calibrated beforehand
- Missing / inconsistent data
- Operation not steady state for 1-2 days
- Laboratory evaluation / sampling problems
- Feedstock changes
Catalyst Selection & Evaluation Methodology

- Technical efficacy of catalyst is settled in several ways:
  - **Paper Study** – supplier provides yield projections of proposed catalyst compared to a base case technology
  - **Commercial References**
  - **Unit trials** – refiners support back to back trials between different catalyst technologies or different catalyst vendors
    - May follow up with post-audit testing with e-cats
  - **Catalyst Laboratory Testing** – internal or external laboratories request fresh catalyst samples. Samples are deactivated and evaluated in lab scale or pilot scale reactors.
  - Often refiners will use a combination of these approaches
FCC Catalyst Selection
Paper Studies and Commercial References

- Paper Studies
  - supplier provides yield projections of proposed catalyst off of a base case technology

- Commercial References for technologies unfamiliar to refiner are often requested

- Pros:
  - Quick, low-cost approach

- Cons:
  - Higher risk
  - Level of inaccuracy for non-incumbent suppliers due to less familiarity of base case
FCC Catalyst Selection
Unit Trials and Post-Audit Assessment

- Refiners support back to back trials between different catalyst technologies
- Analyzing unit data from trials is not always conclusive
  - Feed / operating changes, mass balance issues, etc.
- Laboratory support testing
  - Routine Ecat monitoring
  - Directed testing on unit feed
- Reaction Mix Sample (RMS) testing before & after catalyst change is gaining acceptance
56% of FCCs perform some measure of catalyst testing

- 55% use laboratory scale testing: MAT, ACE and SCT-RT
  - Bulk of this is ACE testing – “Advanced Cracking Evaluation”
- 45% use pilot scale testing: DCR, Arco, internal design

- Catalyst deactivation protocols are highly varied
  - 5% hydrothermal steaming
  - 35% metals impregnation techniques
  - 60% crack on metals

(\% of laboratories – may not always use depending on unit specifics)
Laboratory Catalyst Evaluation Techniques

- Deactivation objective = mimic properties of unit equilibrium catalyst
  - Hydrothermal Steaming - deactivates zeolite
  - Metals impregnation or deposition: (V and Ni species)
  - Many permutations & combinations

- Testing (Cracking)
  - Bench scale – MAT or ACE or SCT-RT
  - Circulating pilot unit

- Data evaluation & scale up
A Suggested Catalyst Deactivation Matrix

Average Metal Concentrations on 126 E-cats

CMDU* catalyst withdrawal

CMDU fresh catalyst addition to mimic Ni aging

E-cat Vanadium Concentration

E-cat Nickel Concentration

Hydrothermal Steaming

Mitchell Impregnation

* Cyclic Metal Deactivation Unit
Example of SEM w/ EDS line scans

Lab Prepared Sample With Impregnated Metals

Commercial E-Cat
Catalyst Deactivation – Contaminant Metals Loading Procedures

CPS: Cyclic Propylene Steaming

- Wet metal impregnation – Mitchell Impregnation
- Redox cycle deactivation $\rightarrow$ C3H6 $\rightarrow$ steam $\rightarrow$ air
- Pros: Faster and more control with total metal deposition
- Cons: Not representative of e-cat metals distribution.

CMDU: Cyclic Metals Deactivation Unit

- Metals added during the cracking cycle
- Redox cycle: cracking $\rightarrow$ regen $\rightarrow$ steam
- Pros: Best model of FCC metal depositio
- Cons: Time / Capacity
Laboratory Catalyst Evaluation
One Example Strategy

- Philosophy for Simulating E-cat in the Laboratory
  - Match H₂ and contaminant coke, NOT metal levels
  - The amount of dehydrogenation that occurs commercially is low
  - Commercial H₂ yield is consistent from unit to unit, 0.15-0.30 wt%

- Rule of thumb for Cyclic Metal Deposition metal levels
  - 25-35% of E-cat nickel
  - 40% of E-cat vanadium
Ecat Results vs. Lab Testing Procedures
How Results Compare

Catalyst metals approx. 1700 ppm V and 800 ppm Ni

Constant C/O of 5

Catalyst metals approx. 1700 ppm V and 800 ppm Ni
Metal Effects on Catalyst Activity/Selectivity
Lab Evaluations are Complex

- Metal dispersion contributes to activity
  - Lab application affects metal dispersion
    - All laboratory techniques exaggerate metal activity
    - Impregnation is the worst
  - Catalyst properties affect metal dispersion
    - High porosity increases metal dispersion in the laboratory
    - No influence on commercial performance
    - A laboratory artifact!

- Metal Age
  - Normal deactivation conditions reduce metal activity = fn(x) (time & temperature)
  - Oxidation – Reduction cycles further reduce metal activity
Elements of Laboratory Catalyst Evaluations

- Deactivation – mimic properties of unit equilibrium catalyst
  - Hydrothermal Steaming - deactivates zeolite
  - Metals impregnation or deposition: (V and Ni species)
  - Many permutations & combinations

- Evaluation
  - Bench scale – ACE, MAT, or SCT-RT
  - Circulating pilot unit
  - Data evaluation & scale up
FCC Catalyst Performance Assessment – from Research to Commercial Application

New Catalyst/Additive R&D

ACE® Reactor

Scale:
Catalyst: 9 - 12 g
Feed: 10 - 20 g
BASF Capability: 5 units

Pilot Circulating Riser Unit

2500 g
0.2 barrel/day
Under construction

Commercial FCC Unit

100+ tons
10,000 + barrels/day
None

BASF Capability:
5 units
Under construction
None
ACE (Advanced Catalyst Evaluation) Fluidized Laboratory Reactor

• ACE® lab scale testing apparatus for FCC catalyst evaluation:
  - Fixed Fluid Bed (FFB) design.
  - Uniform temperature and coke distribution.
  - Automated design allows for quick turnaround time.

• Can be used to troubleshoot & optimize FCCU
  - Flexible and resid capable
  - simulates unit yields

• Excellent precision
Schematic and Process Flow Streams of BASF Circulating Riser Unit
Laboratory Results to Commercial “Data Evaluation & Scale Up”

Laboratory results are not heat balanced

Use laboratory product yields with process simulation model tuned for each FCC unit

Determine expected commercial yields

These processes are complicated – can take over a decade to refine
Summary

- Regular mass balances/test runs are required to properly evaluate the FCC unit operation.
- FCC feed quality and process limits, not the catalyst properties, normally determine the commercial product yields.
- Test Run results should be used with the FCC process limits to optimize the refinery operation.
- Several laboratory catalyst evaluation techniques are available, depending on the unit feedstock quality and operation.
  - Which techniques and how to use are a key knowledge base.
Summary

- Catalyst Deactivation is critical to laboratory testing results
  - Mimicking Ni and V levels in testing are subject to artifacts
    - Unrealistic metals distribution and activity
    - Porosity artifacts
  - CMDU deactivation preferred → target e-cat yields, NOT metal levels
- Catalyst evaluation can be achieved in the lab scale (ACE) or even better in a circulating pilot plant
- BASF has full testing and deactivation capability to service the FCC industry and continue to be a technology leader.