Introduction

• Refineries historically focus most attention on the reactor, riser & fractionation sections of the FCC.
• Focus only applied to the regenerator when necessary due to catalyst losses, afterburn or when environmental regulations required.
• With increasing environmental regulation, paying careful attention to the regenerator is key to avoiding unexpected emissions excursions.
  – The most common causes of SOx, NOx & CO emissions are provided.
  – Regenerator optimization guidelines are included.
Overview

• **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters

• **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum

• **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds

• **Conclusion**

---

**SOx Emissions Control**

• **SOx additives effectively control SOx emissions from the FCC**
  - SOx additives most effective in full burn
  - SOx removal is directly proportional to additive addition rate
    • Amount of removal only dependent on usage rate
    • Steady state emissions of < 5 ppm achievable

• **SOx emissions will correlate with feed sulfur in some units**
  - More commonly correlate better with slurry S
    • Coke S = UF*(slurry S)^1.265

• **Most units process a limited number of feeds**

• **Amount of feed sulfur going to coke varies with feed stock**
  - Regression techniques allow determination of feeds with greatest impact on emissions
SOx Emissions Control

• Feed iron excursions can have significant impact
  – Effect on emissions may be large
  – Half life appears to be short
    • Typically 2-3 days
  – Increasing SOx additive rate sufficient control
  – Identify feed source

• Maximum LCO mode operations
  – Max diesel mode typically includes a reduction in riser outlet & stripper temperatures
  – May lead to insufficient additive regeneration
  – Intercat has developed additive technology effective in LCO mode operations

SOx Emissions Control

• Additive loader failure
  – Select loader supplier based upon highest equipment reliability
  – Loader should be capable of manual additions in case of power outage

• Flue gas analyzer failure
  – Regular maintenance required
  – Flue gas conditioning systems most common cause of poor readings
    • Condensate removal
    • Catalyst fines removal

• SOx emissions are affected by excess oxygen
  – Increasing oxygen leads to reduced emissions
  – Up to approximately 2% excess oxygen
SOx Emissions Control

• Regenerator maldistribution effects on SOx emissions
  – Changes in air & catalyst distribution effect combustion efficiency
  – Maldistribution may result in oxygen rich & lean zones leading to increased SOx
  – Measurements taken with a Reaction Mix Sampling (RMS) device & a gas analyzer
  – Commercial example:
    - Full combustion regenerator
    - Northern half in partial combustion
    - Southern half in full combustion
    - Emissions differ according to oxygen concentration

<table>
<thead>
<tr>
<th>Position</th>
<th>O2 (vol%)</th>
<th>CO (ppm)</th>
<th>SO2 (ppm)</th>
<th>NOx (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.1</td>
<td>2,828</td>
<td>440</td>
<td>152</td>
</tr>
<tr>
<td>#2</td>
<td>2.6</td>
<td>1,429</td>
<td>191</td>
<td>133</td>
</tr>
<tr>
<td>#3</td>
<td>4.3</td>
<td>1,068</td>
<td>83</td>
<td>218</td>
</tr>
<tr>
<td>Fluegas</td>
<td>2.6</td>
<td>83</td>
<td>248</td>
<td>109</td>
</tr>
</tbody>
</table>

SOx Emissions Control

• SOx emissions affected by cat-to-oil
  – CTO influences additive regeneration rate
  – Increased CTO results in increased regeneration and additive effectiveness
  – Platinum based promoters increase oxidation of SO₂ to SO₃ and thereby improve additive efficiency

• Guidelines for minimum SOx emissions:
  1. Increase flue gas excess oxygen
  2. Lower regenerator temperature
  3. Increase regenerator pressure
  4. Increase catalyst circulation rate
  5. Use of platinum based CO promoter
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters

- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum

- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds

- **Conclusion**

---

NOx Emissions Control

- **NOx emissions strongly impacted by excess oxygen in full combustion**
  - Operate with the lowest stable excess oxygen level

- **NOx emissions strongly impacted by CO concentration in partial burn**
  - Operate with lowest stable CO concentration
NOx Emissions Control

- NOx emissions strongly impacted by regenerator maldistribution
  - Analysis techniques:
    - Directly measure regenerator NOx levels with an RMS device & a portable gas analyzer
    - Plotting NOx emissions against delta cyclone outlet temperatures will indicate where maldistribution is occurring
    - Multi-variable linear regression of independent variables

- Antimony for Ni passivation increases NOx in many but not all units
  - Verification of antimony effect recommended
  - Use Ni trapping catalysts where possible

- Platinum based CO promoters
  - Platinum oxidizes nitrogen in coke to NOx
  - Non-platinum promoters effectively control afterburn with lower NOx
    - Typical reductions are 50-70%
    - Beware of over-promotion

- Unit optimization for reduced NOx emissions
  1. Operate a full combustion regenerator at minimum excess oxygen
  2. Operate a partial burn regenerator at minimum CO-to-CO₂ ratio
  3. Avoid platinum based promoters
  4. Carefully monitor antimony injections
  5. Use a non-platinum based promoter for after burn control or a NOx additive

“One refiner having switched to a non-Pt promoter later “found” a bin of Pt-based promoter in the warehouse, delivered it to the unit, began injections, and went out of compliance. Learning point: ensure no Pt-based promoter is in stock after switching to a non-Pt promoter!”
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters

- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum

- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds

**Conclusion**

CO Emissions Control

- This analysis focuses on the full combustion regenerator
  - Most well designed CO boilers will easily control CO emissions

- FCC start-ups are the most common cause of CO emissions
  - Slugs of oil soaked catalyst entering the regenerator may result in a temporary partial burn mode
  - Many operators will add a CO promoter during start-up as a precaution

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>CO</th>
<th>SO</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>1110</td>
<td>7</td>
<td>71</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1112</td>
<td>79</td>
<td>65</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>1355</td>
<td>396</td>
<td>81</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>1401</td>
<td>12</td>
<td>66</td>
<td>57</td>
</tr>
<tr>
<td>Day 2</td>
<td>0824</td>
<td>4</td>
<td>81</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>0931</td>
<td>5</td>
<td>97</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1030</td>
<td>2</td>
<td>105</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1130</td>
<td>1</td>
<td>91</td>
<td>45</td>
</tr>
</tbody>
</table>

Source: J.W. Wilson, AM-03-44
CO Emissions Control

• Maldistribution
  – Maldistribution due to mechanical damage or design flaws will result in increased CO production
  – Poor air & catalyst distribution will result in oxygen and CO rich zones leading to afterburn and possibly CO emissions
  – CO promoters are effective at controlling CO emissions

• Clean feeds
  – Operating low CCR or deeply hydrotreated feedstocks at low regenerator bed temperatures may result CO breakthrough
  – Control responses:
    • Increase bed height & temperature if possible
    • Add CO promoter

Source: J.W. Wilson, AM-03-44

Overview

• SOx emissions
  – Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters

• NOx Emissions
  – Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum

• CO Emissions
  – Start-ups, maldistribution, low CCR & deeply hydrotreated feeds

• Conclusion
Conclusions

- Careful attention to the FCC regenerator will:
  - Maximize combustion efficiency
  - Minimize the probability of unexpected flue gas emissions

- The time commitment by the process engineer is minimal if these techniques are incorporated into daily monitoring routines

- Swift determination of the root cause of flue gas emissions should be enhanced using these techniques

Ray Fletcher ~ rfletcher@intercatinc.com
Martin Evans ~ mevans@intercatinc.com