Improve FCCU profitability by selecting the proper catalyst

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New challenges for FCC Units

- With the greater processing of heavy crude oils in refineries, the importance of fluid catalytic cracking unit has been increased;

- Metals content in heavy feeds is one of the limiting factors in FCCUs, as increased levels of metals lead to high coke and dry gas yields;

- However, processing heavy oil streams in FCCUs also leads to increased distillate yields and improved margins;

- Lukoil Petrotel is not exception of the world trends.
Petrotel-Lukoil FCCU is processing a non-hydrotreated feed (VGO + HCGO) with high contaminants content (S, N, Ni and V):

<table>
<thead>
<tr>
<th>No.</th>
<th>Properties</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density</td>
<td>Kg/m³</td>
<td>916 – 930</td>
</tr>
<tr>
<td>2</td>
<td>Sulphur</td>
<td>%</td>
<td>1.6 - 1.8</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen</td>
<td>ppm</td>
<td>1400 - 1900</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>ppm</td>
<td>≤ 0.66</td>
</tr>
<tr>
<td>5</td>
<td>V</td>
<td>ppm</td>
<td>≤ 1.45</td>
</tr>
<tr>
<td>6</td>
<td>IFB / FBP</td>
<td>ºC</td>
<td>320/575</td>
</tr>
<tr>
<td>7</td>
<td>Coke Conradson</td>
<td>%wt</td>
<td>0.4 – 1.2</td>
</tr>
</tbody>
</table>
Ni and V contamination of FCC e-cat

Processing a heavy feed led to contamination/poisoning of e-cat with Nickel and Vanadium:
Ni and V is concentrated in the >540°C Cut: VGO (Dist. 90% = 540°C, FBP = 575°C) and Vacuum Residue (DCU feed).
Study of Ni and V distribution of refinery process flows

- **Crude Oil Feed (Urals+Siberian+Kirkuk)**
  - Ni: 11.4 ppm
  - V: 28.06 ppm

- **DAV**
  - Gasoline
    - Ni: 0.17 ppm
    - V: 0.023 ppm
  - Gas Oil
    - Ni: 0.11 ppm
    - V: 0 ppm
  - VGO
    - Ni: 0.73 ppm
    - V: 1.92 ppm
  - Vacuum Residue
    - Ni: 60 ppm
    - V: 165 ppm

- **FCC**
  - HCGO
    - Ni: 0.31 ppm
    - V: 0.21 ppm
  - Slurry
    - Ni: 3.2 ppm
    - V: 7.7 ppm
  - HCO
    - Ni: 1.71 ppm
    - V: 5.51 ppm

- **Contamination of FCC e-cat with Ni and V**
  - Gasoline
    - Ni: 0 ppm
    - V: 0 ppm
  - LCO
    - Ni: 0 ppm
    - V: 0.044 ppm
  - Slurry
    - Ni: 0 ppm
    - V: 0 ppm
  - HCO
    - Ni: 0 ppm
    - V: 0.044 ppm

- **Delayed Coker Unit**
  - Coke
    - Ni: 129.9 ppm
    - V: 653.1 ppm
In 2014 Petrotel-Lukoil selected BASF’s NaphthaMax® II-HM FCC catalyst with Low NOx CO Promoter;

Since 2014 BASF reformulated the catalyst 3 times to optimize;

By working together Petrotel-Lukoil team and BASF, the refinery was able to sustain beneficial FCC performance despite significant feed quality variations;

To mitigate negative effect of high metal levels (Ni and V) in April 2017 our catalyst supplier delivered high quality E-cat;

In 2018 was selected BASF Aegis LPN 21 catalyst.
### FCC e-cat contamination with Ni and V

<table>
<thead>
<tr>
<th>No.</th>
<th>FCC catalyst</th>
<th>Ni + V</th>
<th>FACT wt%</th>
<th>TSA m²/g</th>
<th>ZSA m²/g</th>
<th>REO wt.%</th>
<th>0-20µ</th>
<th>0-40µ</th>
<th>APS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh catalyst</td>
<td>0</td>
<td>76</td>
<td>295</td>
<td>185</td>
<td>1.5</td>
<td>2</td>
<td>12</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>FCCU e-cat</td>
<td>5033</td>
<td>65.5</td>
<td>135</td>
<td>90</td>
<td>1.5</td>
<td>0</td>
<td>4</td>
<td>78</td>
</tr>
</tbody>
</table>

**Nickel:**
- Deposits on catalyst particles;
- Dehydrogenation activity leading to increased hydrogen and coke yields.

**Vanadium:**
- Deactivate the catalyst causing activity reduction;
- Increases hydrogen and coke yield;
- Destroys the zeolite (especially in the presence of Na).
In order to reduce metal contamination the refinery implemented the following solutions:

1. E-cat flushing of FCCU inventory to replace the contaminated e-cat;

2. Optimization of fresh catalyst addition. Fresh catalyst dosage rate was increased from 0.6 to 1 kg/t in order to maintain constant the level of Ni and V on FCCU e-cat;

3. Reformulation of fresh catalyst in order to increase its resistance at high Ni and V contamination.
E-cat flushing of FCCU inventory

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<tr>
<th>No.</th>
<th>FCC catalyst</th>
<th>FACT wt.%</th>
<th>TSA m²/g</th>
<th>ZSA m²/g</th>
<th>REO wt.%</th>
<th>0-20µ</th>
<th>0-40µ</th>
<th>APS</th>
<th>CO Promoter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh catalyst</td>
<td>76</td>
<td>295</td>
<td>185</td>
<td>1.5</td>
<td>2</td>
<td>12</td>
<td>75</td>
<td>Pd</td>
</tr>
<tr>
<td>2</td>
<td>FCCU e-cat</td>
<td>65.5</td>
<td>135</td>
<td>90</td>
<td>1.5</td>
<td>0</td>
<td>4</td>
<td>78</td>
<td>Pd</td>
</tr>
<tr>
<td>3</td>
<td>Proposed e-cat</td>
<td>73.3</td>
<td>173</td>
<td>118</td>
<td>1.74</td>
<td>1</td>
<td>9</td>
<td>75</td>
<td>Pt</td>
</tr>
</tbody>
</table>

Advantages of using the selected e-cat for flushing:
✓ Lower cost for procurement in comparison with fresh catalyst;
✓ Good quality in comparison with other e-cat types: FACT, TSA, ZSA, REO, APS;
✓ The selected e-cat is promoted with ZSM 5.

Disadvantages of using the selected e-cat for flushing:
➢ The e-cat is pre-blended with Pt-CO Promoted which will have a negative impact on NOx emissions.
The refinery decided to inject the proposed e-cat in 6 different batches in order to replace the contaminated catalyst from FCCU inventory but to avoid the increasing of NOx in Flue Gas.

Starting the dosage of BASF Aegis LPN 21
E-cat flushing of FCCU inventory

Dosing a catalyst pre-blended with Pt-CO Promotor increased the NOx emissions in FCCU Flue Gas up to 220 mg/Nm3 (below the maximum allowed limit imposed by Environmental Regulation – 300 mg/Nm3).
Effect achieved by reducing Ni and V content on e-cat

<table>
<thead>
<tr>
<th>FCC UNIT Products</th>
<th>Unit</th>
<th>Material Balance 5030 ppm Ni+V</th>
<th>Material Balance 2640 ppm Ni+V</th>
<th>Δ -2390 ppm Ni +V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas</td>
<td></td>
<td>6.93</td>
<td>5.98</td>
<td>-0.95</td>
</tr>
<tr>
<td>Propane</td>
<td></td>
<td>1.57</td>
<td>1.78</td>
<td>+0.20</td>
</tr>
<tr>
<td>Propylene</td>
<td></td>
<td>4.22</td>
<td>4.56</td>
<td>+0.34</td>
</tr>
<tr>
<td>Total C4</td>
<td>wt.%</td>
<td>8.37</td>
<td>10.60</td>
<td>+2.24</td>
</tr>
<tr>
<td>Gasoline</td>
<td></td>
<td>44.58</td>
<td>46.05</td>
<td>+1.47</td>
</tr>
<tr>
<td>LCO</td>
<td></td>
<td>19.42</td>
<td>17.31</td>
<td>-2.11</td>
</tr>
<tr>
<td>HCO</td>
<td></td>
<td>9.16</td>
<td>8.26</td>
<td>-0.90</td>
</tr>
<tr>
<td>Coke</td>
<td></td>
<td>5.44</td>
<td>5.15</td>
<td>-0.29</td>
</tr>
<tr>
<td>Losses</td>
<td></td>
<td>0.31</td>
<td>0.31</td>
<td>0.00</td>
</tr>
<tr>
<td>Conversion</td>
<td>wt.%</td>
<td>71.42</td>
<td>74.43</td>
<td>+3.01</td>
</tr>
</tbody>
</table>

Economic Effect $/t feed 1.92

*Note: the Economic Effect was calculated based on refinery RPMS model.*
The refinery organized a tender to select a more metal resistant catalyst (higher zeolite and REO content) for a 3 year contract.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fresh catalyst characteristics</th>
<th>unit</th>
<th>Naphtha Max II</th>
<th>Aegis</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FACT</td>
<td>wt.%</td>
<td>76</td>
<td>77</td>
<td>+1</td>
</tr>
<tr>
<td>2</td>
<td>ZSA</td>
<td>m²/g</td>
<td>185</td>
<td>205</td>
<td>+20</td>
</tr>
<tr>
<td>3</td>
<td>MSA</td>
<td>m²/g</td>
<td>110</td>
<td>85</td>
<td>-25</td>
</tr>
<tr>
<td>4</td>
<td>TSA</td>
<td>m²/g</td>
<td>295</td>
<td>290</td>
<td>-5</td>
</tr>
<tr>
<td>5</td>
<td>REO</td>
<td>m²/g</td>
<td>1.5</td>
<td>1.8</td>
<td>+0.3</td>
</tr>
<tr>
<td>6</td>
<td>Low NOx-CO Promoter</td>
<td></td>
<td>Mandatory</td>
<td>Mandatory</td>
<td></td>
</tr>
</tbody>
</table>
Cyclones failure (cracks, plugging, etc) are causing massive e-cat losses which consequently lead to FCCU emergency shut-down;

If immediate unit shut-down is not possible than is needed to increase the catalyst addition rate in order to compensate the e-cat losses from FCCU system;

To reduce the operational cost it is recommended to maintain the regenerator catalyst level by dosing e-cat instead of fresh catalyst.
Usage of e-cat in FCCU emergency situation

ECONOMIC LOSSES
Utilization of e-cat in emergency situation caused by cyclones failure

Cyclones failures can be detected easily by doing the following actions:

- Monitoring the FCCU regenerator level;
- Evaluation of e-cat quality: absence of e-cat fines is caused by cyclones inefficiency/failure;
- Monitoring of particulates content in Flue Gas (if there is an on-line analyzer on Flue Gas stack);
- Monitoring the quantity of catalyst collected in Flue Gas Treatment Unit (Wet Scrubbing System, ESP, etc).
Usage of e-cat in emergency situation caused by cyclones failure

- The FCCU engineers noticed a decreasing of regenerator level in the conditions of maintaining the same fresh catalyst addition rate;
- Increasing of APS and complete loss of 0 - 45μ fines;
- Increasing of catalyst quantity collected in BELCO Flue Gas Treatment Unit;
- FCCU shut-down for regenerator inspection was planned in July (in order to achieve the Production Planning targets);
During FCCU regenerator inspection it was found that 2 cyclones (2\textsuperscript{nd} stage) were plugged.
In case of cyclones failure it is recommended to compensate the catalyst losses by dosing e-cat instead of fresh catalyst.

<table>
<thead>
<tr>
<th>Filter cake collected in BELCO Unit (35% catalyst content)</th>
<th>Catalyst losses</th>
<th>Economic Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>tons</td>
<td>tons</td>
<td>$</td>
</tr>
<tr>
<td>211</td>
<td>74</td>
<td>203,382</td>
</tr>
</tbody>
</table>

*Note: The procurement cost presented for catalyst are estimative and can vary depending on catalyst supplier or the type of catalyst supplied.*
Conclusions

- Processing a heavy, non-hydrotreated feed (VGO+HCGO) can lead to the contamination of FCC equilibrium catalyst with Ni and V;
- Ni and V has a poisoning effect on FCC e-cat and increases the hydrogen and coke yields. Also vanadium deactivate the catalyst causing activity reduction;
- The most efficient method that can be implemented for a rapid reduction of Ni and V content is e-cat flushing (taking into consideration the procurement cost);
- Reduction of Ni and V content with -2394 ppm by e-cat flushing increased the FCCU conversion with 3.01 wt. %. Consequently were increased the yields in Propane (+0.20%), Propylene (+0.34%), C4 Cut (+2.24%) and Gasoline (+1.47%). Also were reduced the yields in Dry Gas (-0.95%), LCO (-2.11%), HCO (-0.90%) and Coke (-0.29%);
- The Economic Effect achieved by reducing Ni and V contamination was estimated by the refinery at ~1.92 $/t feed;
Conclusions

- It is important to evaluate the quality of the e-cat proposed to be used for flushing in order to not affect the FCC efficiency;
- To avoid the continuous accumulation of Ni and V it is recommended to increase the catalyst dosage rate and adapt it to the feed quality;
- Reformulation and/or selection of a more metal resistant catalyst;
- Cyclones failure can cause massive e-cat losses which consequently lead to FCCU emergency shut-down. If immediate unit shut-down is not possible it is recommended to compensate the catalyst losses by dosing low cost e-cat instead of fresh catalyst;
- In a refinery case (2 cyclones plugged) the economic effect achieved by dosing e-cat instead of fresh catalyst in order to maintain in operation the FCCU (until the planned shut-down) was estimated at ~200,000 $;
- All refineries should have an e-cat stock for FCCU emergency situations.
Thank you for your attention!