Approximately half of fluidised catalytic cracking (FCC) units worldwide process feedstock containing residue (i.e. resid feeds). In regions where access to light crudes or tight oil is limited, the tendency to process resid feeds is even greater. In these regions, this trend is also related to the necessity to improve the profitability of the FCC unit by processing lower cost resid feeds, which leads to the strategic target of utilising catalysts that can provide an increased flexibility to handle such challenging feeds. Resid feeds typically contain contaminant metals including nickel (Ni), vanadium (V), iron (Fe), and other metals that catalyse a variety of unwanted secondary reactions in the FCC unit. Even small amounts of these contaminant metals in the feed deposit cumulatively on the catalyst, which is a major concern for the refining industry. Nickel specifically being a highly active dehydrogenation catalyst presents a considerable challenge as it significantly increases hydrogen (H₂) and

Shaun Pan, Alexis Shackleford, Robert McGuire Jr., Gary M. Smith and Bilge Yilmaz, BASF Corporation, USA, explain how operators can increase FCC unit profitability using catalysts from boron based technology.
such as slurry heat exchanger fouling. The use of specialty aluminas for Ni trapping also reduces H₂ and coke. However, its efficacy is limited by the limited mobility of Ni. When analysing equilibrium catalyst (Ecat) particles for Ni, Ni is concentrated on the outer section of the Ecat, demonstrating that it has very low mobility under FCC conditions. In order to quantify intraparticle mobility of contaminant metals, a new method was developed which utilises scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and/or electron probe micro analysis (EPMA) data of cross-sectional areas of catalyst particles; and comparison of the amount of contaminant metal on the outer stages versus at the core of the microsphere gives the peripheral deposition index (PDI) value. For Ni, the PDI values reported are typically rather high, confirming its very low mobility. Nickel is passivated when it is in close proximity to the trapping alumina. The low mobility of Ni and the stationary nature of the trapping alumina in the catalyst particle leads to a non-optimal passivation of Ni. Resid feeds also contain higher amounts of aromatics and Conradson carbon residue (CCR) compared to vacuum gas oil (VGO) feeds. Due to these large compounds, optimised catalyst pore structure is critical to convert the heavier material to more valuable products while limiting coke formation.

BASF has developed a new catalyst technology platform, boron based technology (BBT), that offers greater flexibility and profitability to refiners processing resid feeds by minimising the negative impact of contaminant metals. The enhanced Ni tolerance is achieved by the boron compound loaded on a special inorganic support that is introduced into the catalyst. Under FCC unit conditions, this boron compound is mobile and will seek out and passivate the Ni, inhibiting its activity in dehydrogenation reactions thus improving liquid yield. And unlike Sb, boron does not increase NOX emissions. Combining the novel use of boron with a pore architecture that minimises diffusional limitations of heavy feed molecules, this new technology allows the lowest H₂ and coke yields coupled with higher valuable liquid hydrocarbon yields. If up against a wet gas compressor limit, reducing the H₂ will allow a commercial unit to increase resid feed rate or operating severity. Improved coke selectivity can allow a unit to process more resid or lower the regenerator temperature, thus increasing the operational flexibility and the unit liquid yields. Another option for units in partial burn is to decrease the CO production, which will increase liquid yield.

The BBT platform offers a variety of catalysts to refiners that are tailored for the yields and metals passivation needs of their resid FCC units. Advanced cracking evaluation® (ACE) results of a BBT catalyst loaded with 3000 ppm Ni and 3000 ppm V were previously published in Hydrocarbon Engineering showing a comparison with BASF’s heavy resid catalyst, Flex-Tec™. The two catalysts were deactivated following various common procedures at identical metals loading levels. As demonstrated in that study, the BBT catalyst results in significantly lower H₂ and coke yields with improved gasoline and LCO yields for all deactivation methods. In this contribution, the results from one of the early refinery trials of a BBT catalyst in a resid FCC unit demonstrate the commercial benefits of this new technology.
Unit performance
BASF’s Borocat FCC catalyst is the first commercialised catalyst off the BBT platform. One of the early commercial trials of Borocat was commenced in 2014. The FCC unit is located in the USA and runs a moderate resid feed with 20 - 22 API gravity and 1 - 2% CCR, with Ecat metals of ~2300 ppm Ni and ~3800 ppm V. The unit configuration includes a catalyst cooler to control regenerator temperature. The unit uses flush catalyst and Sb injection to control H2 production and ZSM-5 for light olefins production. During the trial, the flush catalyst usage pattern was maintained at a similar level as prior to the trial to minimise any differences. The main objectives for the unit are to minimise the amount of H2 produced as well as to maximise conversion and bottoms upgrading. The customer wanted to take advantage of Borocat to reduce the detrimental impact of Ni and improve operating flexibility and unit profitability. Prior to the Borocat trial, the unit was using BASF’s Flex-Tec catalyst, which contains specialty alumina for Ni passivation.

Prior to the start of the Borocat trial, BASF used the customer focused technical support services (TSS)\(^6\) and collaborated with the refinery to standardise the unit operating data and further improve the mass balance of the FCC unit. Ecat samples were sent to BASF for physicochemical characterisation as well as catalytic evaluation in ACE. This is a standardised testing method using a fixed fluidised bed, which simulates the riser performance. All Ecat samples were run under the same conditions (feed, temperature, catalyst to oil ratio, etc.), providing a good basis for comparison. In addition, samples of FCC regenerator fines, feedstock, slurry and scrubber water were sent to BASF for analysis to closely monitor the unit operation during the trial.

Catalytic evaluation of shipment retains
Retains of fresh catalyst shipments of Flex-Tec and Borocat were collected, loaded with contaminant metals (Ni and V), and deactivated in the laboratory environment using cyclic propylene steaming (CPS). The metal loading levels on the catalyst were 2300 ppm Ni and 3800 ppm V, similar to the historical average Ecat metal levels in the unit. The deactivated catalysts were tested in an ACE unit with the feedstock obtained from the FCC unit.

As shown in Table 1, at a constant conversion of 75 wt.%, Borocat reduced the H2 and coke yields by 26% and 16%, respectively, compared to Flex-Tec. The lower H2 and coke yields can be attributed to the unique ability of the boron compound to effectively passivate Ni. The improvements in H2 and coke selectivity translated into a higher gasoline yield (+3%). Additionally, the Borocat catalyst improved bottoms upgrading, increasing the LCO yield by 1% while reducing the slurry yield by 2%.

Equilibrium catalyst data review
As discussed above, Ecat samples were routinely collected and sent to BASF for testing. The equivalent Ni level on Ecat, which is calculated by the conventional Ni+V/4-4/3*Sb formula, represents the equivalent dehydrogenation activity of the metals on the Ecat samples. During the trial, the equivalent Ni level slightly
Figure 6. Slurry API gravity decreased significantly during the Borocat trial.

Table 2. Projected unit yields and profitability for Flex-Tec and Borocat at constant operating conditions

<table>
<thead>
<tr>
<th></th>
<th>Flex-Tec</th>
<th>Borocat</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate, 1000 bpd</td>
<td>38.1</td>
<td>38.1</td>
<td>0.0</td>
</tr>
<tr>
<td>API gravity</td>
<td>19</td>
<td>19</td>
<td>0.0</td>
</tr>
<tr>
<td>ROT, °F</td>
<td>974</td>
<td>974</td>
<td>0.0</td>
</tr>
<tr>
<td>Delta coke (wt/wt)</td>
<td>0.71</td>
<td>0.64</td>
<td>-0.07</td>
</tr>
<tr>
<td>Conversion, wt.%</td>
<td>69.0</td>
<td>69.4</td>
<td>+0.4</td>
</tr>
<tr>
<td>H₂, wt.%</td>
<td>0.15</td>
<td>0.10</td>
<td>-0.05</td>
</tr>
<tr>
<td>LPG, vol.%</td>
<td>27.8</td>
<td>28.7</td>
<td>+0.9</td>
</tr>
<tr>
<td>Gasoline, vol%</td>
<td>52.5</td>
<td>53.0</td>
<td>+0.5</td>
</tr>
<tr>
<td>LCO, vol%</td>
<td>12.1</td>
<td>12.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>Slurry, vol.%</td>
<td>7.7</td>
<td>7.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Profitability</td>
<td>Base</td>
<td>+$0.32/bbl (winter)</td>
<td>0.38/bbl (summer)</td>
</tr>
</tbody>
</table>

decreased from 2700 ppm to 2500 ppm and the reduction was within the normal operating window for the unit.

ACE H₂ to methane ratio (H₂/CH₄), which is an indicator of the H₂ selectivity of the Ecater, was plotted against equivalent Ni level to compare the H₂ selectivity between Flex-Tec and Borocat. As shown in Figure 1, Borocat reduced the H₂ selectivity of the Ecater, was plotted against equivalent Ni level. The reduction in H₂ again demonstrated the superior ability of Borocat to crack bottoms while improving the incremental yield of LCO was highly attractive for unit economics. LCO is the most valuable product for the refinery in the winter and second most valuable during the summer time. The incremental improvement in LCO yield led to additional profitability improvement for the unit.

To monitor the introduction of Borocat catalyst into the unit and the new metals passivation chemistry associated with it, an immobile tracer element was also incorporated into the catalyst and the concentrations of the tracer element and boron in the Ecater were closely followed. As the Ecater inventory transitioned to Borocat, the content of the tracer element and boron in Ecater increased gradually. The weight ratio of tracer to boron in Ecater was calculated and compared to the ratio in the fresh catalyst shipment. As shown in Figure 4, the Ecater tracer/boron ratio during the trial was consistent with the target value. Additionally, the tracer/boron ratios in the regenerator and slurry fines were measured and they were again consistent with the target ratio. The consistent tracer/boron ratio indicated that the boron was retained in the Ecater inventory, and no preferential loss of boron was observed.

Operating data review

The benefit of Borocat in reducing H₂ yield was demonstrated in unit operating data, confirming the Ecater ACE lab data. As shown in Figure 5, the commercial H₂/CH₄ versus Ecater equivalent Ni level shows that Borocat gives a -25% reduction in H₂/CH₄ ratio compared to Flex-Tec. The reduction in H₂ again demonstrated the superior ability of the boron based technology to passivate Ni and reduce the overall dehydrogenation activity in the unit.

The operating data confirms that Borocat gives improved bottoms upgrading and high LCO selectivity. Borocat also gives higher activity allowing the unit to increase conversion. The higher conversion and the bottoms upgrading benefits of BBT resulted in low slurry yield and a significant decrease in the slurry API gravity. As shown in Figure 6, the slurry API gravity decreased to -4, the lowest level for the unit over the past year and the unit’s minimum slurry gravity limit.
Due to the changes in the operating conditions during the trial, KBC FCC-SIM was employed to normalise the operating conditions and demonstrate the yield and profitability improvements delivered by BBT. As shown in Table 2, at constant operating condition, Borocat decreased the operating delta coke through more effective passivation of contaminant metals leading to a significant reduction in contaminant coke. The reduction of contaminant coke enabled a higher catalyst to oil ratio to be run in the unit and thus a higher unit conversion. Unit H₂ make decreased by 33% from 0.15 wt.% to 0.1 wt.%. LPG and gasoline yields increased by 0.9 vol.% and 0.5 vol.%, respectively. Slurry yield decreased by 0.3 vol%. Despite the higher conversion, LCO yield was maintained for improved LCO selectivity. Driven by the slurry upgrading and improvements in H₂ and coke selectivity, the unit profitability improvement was calculated to be US$0.32/bbl in the winter time and US$0.38/bbl in the summer time, based on the seasonal economics.

**Conclusion**

The new catalyst technology platform developed by BASF, BBT, offers greater flexibility and profitability to refiners processing resid feeds by minimising the negative impact of contaminant metals and providing higher valuable liquid hydrocarbon yields. The BBT technology platform offers a variety of catalysts to refiners that are tailored for the yields and metals passivation needs of their resid FCC units. Performance of the first catalyst from the BBT platform, Borocat, in a commercial FCC unit was studied in detail and compared to the performance of the previous catalyst in the unit (Flex-Tec) that utilises a traditional specialty alumina based Ni trapping technology. Use of Borocat in the refinery resulted in significantly lower H₂ and coke yields, improved liquid product yields and improved unit economics. These findings demonstrate the enhanced metals tolerance and improved catalytic performance of the BBT platform compared to conventional metals passivation technologies.

**References**

1. BASF Market Share database 2015.