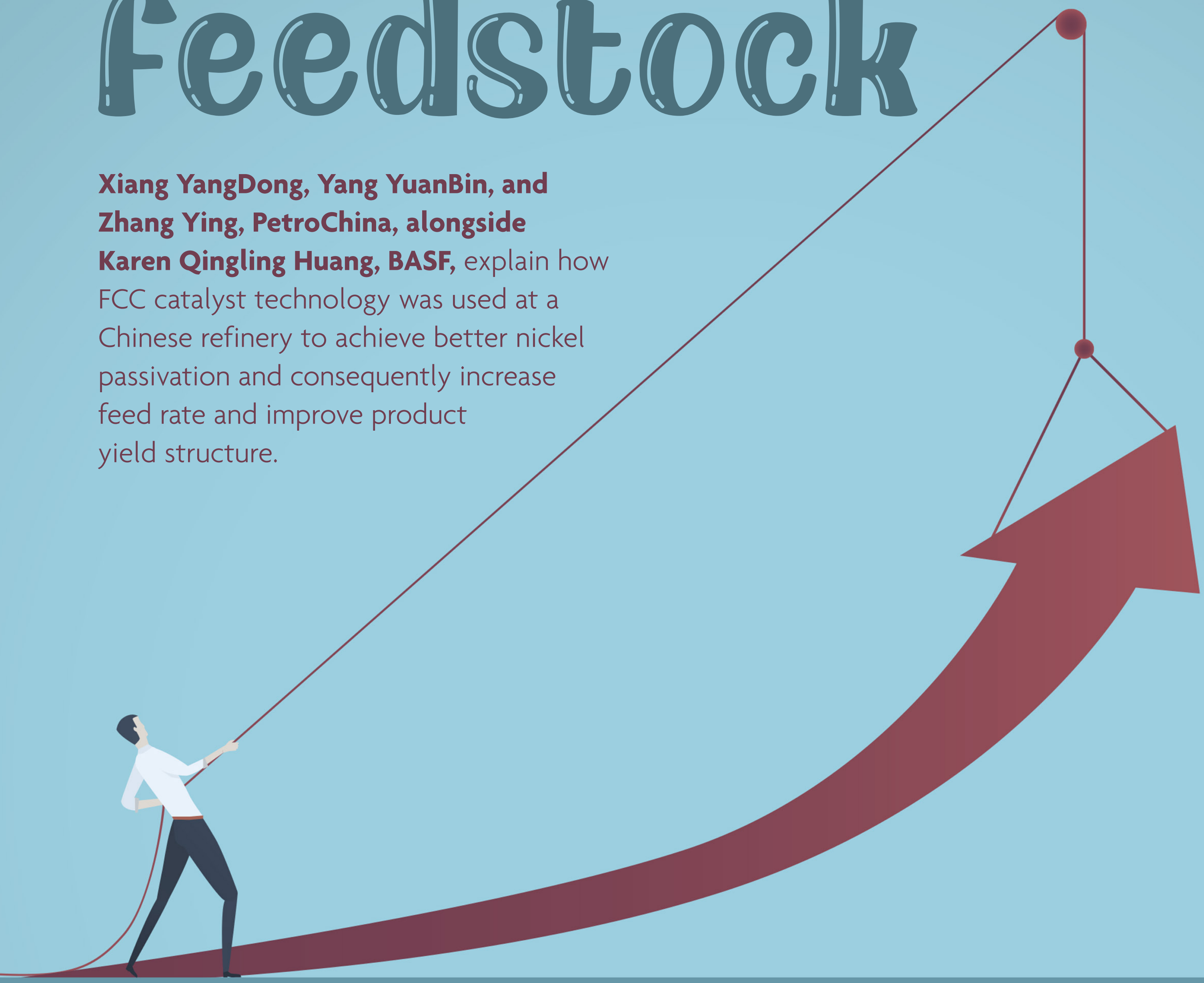
Tackling high nickel feedstock



Xiang YangDong, Yang YuanBin, and Zhang Ying, PetroChina, alongside Karen Qingling Huang, BASF, explain how FCC catalyst technology was used at a Chinese refinery to achieve better nickel passivation and consequently increase feed rate and improve product yield structure.

PetroChina's Liaohe refinery in the Liaoning province of China operates a residue fluidised-bed catalytic cracking (RFCC) unit, which has a two-stage regenerator with catalyst coolers. The feedstock is mostly atmospheric residue derived from crudes from Shengyang province, China, with coker gas oil (CGO) making up the remaining ~10%. The combined feedstock to the RFCC unit has a high Conradson carbon residue (CCR) content (typically 4 – 6 wt%), a very high nickel (Ni) content (typically 10 – 20 ppm), and a very low vanadium content (typically < 1 ppm).

Ni is well known for its high dehydrogenation activity, which leads to increased hydrogen (H_2) and coke yield. High volumetric flow from the low molecular weight H_2 may lead to wet gas compressor and gas concentration unit capacity limits. In addition, in most FCC units H_2 is routed to the

Table 1. Feed qualities before and during BoroCat trial

	Unit	Before trial	During trial
Density	kg/m^3	904.9	906.2
CCR (%)	wt%	5.3	5.2
Fe	ppm	4.35	4.5
Ni	ppm	17.5	17.8
Na	ppm	2.45	2.4
Paraffins	%	75.4	74.9
Aromatics	%	17.6	17.6

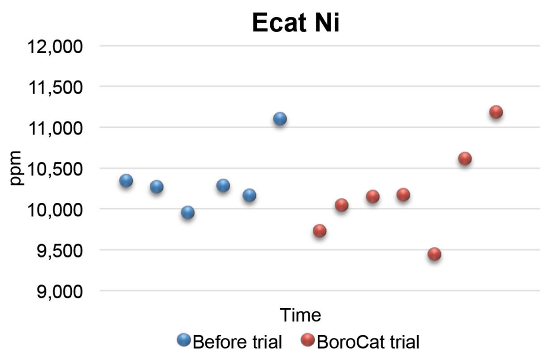


Figure 1. Ecat Ni before and during BoroCat trial.

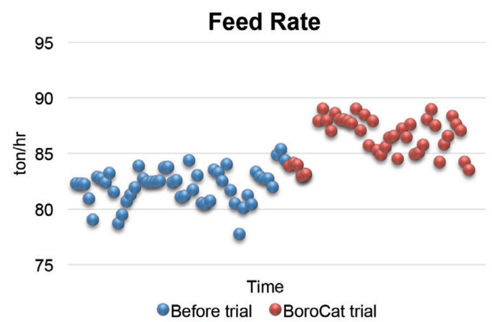


Figure 2. Feed rate to RFCC unit before and during BoroCat trial.

Table 2. Normalised product yields and properties based on operating data

	Unit	Before BoroCat trial	BoroCat trial	Absolute delta	Relative delta (%)
Dry gas	wt%	5.51	4.73	-0.78	-14.2
LPG	wt%	8.26	8.31	0.05	0.7
Gasoline	wt%	44.4	44.84	0.44	1
LCO	wt%	29.89	30.6	0.71	2.4
DCO	wt%	4.39	4.38	-0.01	-0.3
Coke	wt%	7.55	7.15	-0.41	-5.4
H_2/CH_4	-	3.66	3.46	-0.2	-5.5
DCO density	kg/m^3	1000	1009.8	9.8	1

refinery fuel gas system, where it has a low economic value. Another product of the dehydrogenation reaction is coke, which is also a low value product with the potential to constrain regenerator operation in areas such as regenerator air, regenerator temperatures, or catalyst cooler duty.

Conventional Ni passivation techniques include the injection of antimony (Sb) and the incorporation of Ni-trapping specialty alumina into the FCC catalyst. While Sb injection can be effective in reducing the dehydrogenation effects of Ni, it can also poison carbon monoxide (CO) combustion promoters and can lead to increased NO_X emissions. The use of specialty aluminas for Ni-trapping also reduces H_2 and coke, but its efficacy is limited by the very low mobility of Ni. Comparing the amount of contaminant metal concentrated on the surface against the core gives the peripheral deposition index (PDI) value.[1,2] The measured PDI values for Ni are typically high, confirming its very low mobility.[1,2] Due to its low mobility under FCC conditions, Ni is typically concentrated on the outer section of the equilibrium catalyst (Ecat) and can only be passivated when it is in close proximity to the alumina. The low mobility of Ni and alumina in the catalyst particle leads to insufficient passivation of Ni.

As Liaohe's RFCC unit runs against wet gas compressor and catalyst cooler limits, addressing the adverse effect of Ni is key for the unit to achieve greater profitability.

Catalyst technology

Boron based technology (BBT) is a catalyst technology platform developed by BASF that is different from conventional Ni passivation techniques, such as injection of Sb and the incorporation of Ni-trapping specialty alumina into the FCC catalyst. The enhanced Ni passivation ability of BBT is achieved through the loading of the boron compound on to 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 and thus improving liquid yield.

Combining this use of boron with a pore architecture that minimises diffusional limitations of heavy feed molecules, BBT enables the lowering of H_2 and coke yield coupled with higher valuable liquid hydrocarbon yields. If up against a wet gas compressor limit, reducing the H_2 yield will allow a 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 operational profitability and flexibility.

Application at the Liaohe refinery

The Liaohe refinery saw the potential in BBT to address the RFCC unit constraints resulting from high Ni feedstock and started a trial of BoroCat – the first catalyst based on the BBT platform that is designed for high conversion. The specific catalyst properties were customised to suit Liaohe's RFCC unit conditions after extensive discussion between the refinery and BASF. The trial started in December 2018, displacing the incumbent non-BASF catalyst in the system. Feed qualities (Table 1) were similar before and during the trial, enabling a relatively straightforward comparison in the unit.

During the trial, the catalyst addition rate was maintained at 1.81 kg catalyst/t feedstock. With similar Ni content in the feedstock, Ecat Ni before and during the BoroCat trial was similar at around 10 000 ppm with +/- 10% variation (Figure 1).

The unit responded to BoroCat in several positive ways. The significant reduction of H_2 and coke yield relieved the constraints on the wet gas compressor and catalyst coolers, allowing the feed rate to increase by ~6.9% (Figure 2).

The reactor temperature is adjusted to produce decanted oil (DCO) with properties that make it suitable as feedstock for needle coke production. During the trial, the unit was able to lower the reactor temperature by ~10˚C from the baseline prior to the trial and achieve similar DCO yield and properties. This was due to the bottoms cracking capability of BoroCat.

Despite higher unit throughput and lower reactor temperature, BoroCat delivered improved product yield distribution (Table 2). Low value products such as dry gas and coke were reduced. Both coke and H_2/methane (CH_4)were reduced by more than 5% relative to the baseline, demonstrating a significant reduction in the damaging hydrogenation activity of Ni. On the other hand, the yield of valuable products such as gasoline and LCO increased. DCO yield remained similar, with DCO density being slightly higher during the trial.

Based on the Liaohe refinery's estimation, the improvement in product yield structure generated an incremental value of ~US$0.71/bbl net off catalyst cost. Furthermore, higher throughput to the RFCC unit was achieved, providing a second layer of economic benefits delivered by BoroCat.

Conclusion

BBT provides enhanced Ni tolerance via the use of mobile boron compounds to hunt for and passivate Ni molecules.

A trial of BoroCat FCC catalyst was conducted in the RFCC unit of PetroChina's Liaohe Refinery, which processes very high Ni feedstock, leading to Ecat Ni of around 10 000 ppm. BoroCat delivered the promised improvement in Ni passivation, as evidenced by a lower H_2/C_1 ratio and coke yield compared to the incumbent catalyst. This in turn relieved unit constraints, allowing the unit to increase feed rate by ~6.9%. Even at higher throughput, BoroCat delivered an improved yield structure, as evidenced by higher gasoline and LCO yields and the same DCO yield. Overall, the unit benefited from BoroCat through a margin improvement of ~US$0.71/bbl and additional feedstock processing. The results from the trial have shown how a RFCC unit processing high Ni feedstock can benefit from BBT.

References

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