Continued gains in FCC pretreating: part I

Case studies show where users are achieving significant gains in system capability, flexibility and economics. Also discussed are catalyst system loadings that reduce the need for low-activity demetallisation catalysts traditionally required to process heavier feeds

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Within the context of the drive for clean fuels, shifting product patterns and heavier feeds, Criterion's proprietary Ascent catalysts are being increasingly used for their ability to:

— Show greater stability in more severe operations at higher temperatures and lower pressures

— Be employed flexibly to select the optimum fluid catalytic cracking (FCC) pretreat operating strategy to maximise FCC margins

— Process heavier feeds with more contaminants

— Desulphurise, denitrify and saturate to a high degree using lower amounts of hydrogen

— Produce ultra-low sulphur diesel (ULSD) and low-sulphur gasoline

— Work effectively and in conjunction with mild hydrocracking catalysts in the more severe operating regimes employed for mild hydrocracking.

Clean fuels success

In complex and integrated refineries, meeting stringent gasoline and ULSD specifications has greatly increased the impact of process unit interactions. This move to clean fuels, continued increases in crude pricing as well as shifts in demand between motor gasoline and diesel have required competitive refiners to re-evaluate how to best utilise both available refining assets and limited capital budgets.

In vacuum gas oil (VGO) processing, increases in hydroprocessing performance have been achieved with the Ascent family of catalysts. In today's refining environment of increasing feed difficulty and contracting profit margins, these improvements in catalytic performance have allowed refiners to review how to best utilise their refining assets. Refiners who are using the Ascent technology to pretreat the feed for FCC operations are realising significant benefits, from extended periods between unit shutdowns, increases in refinery yields to the capability to process more difficult feeds.

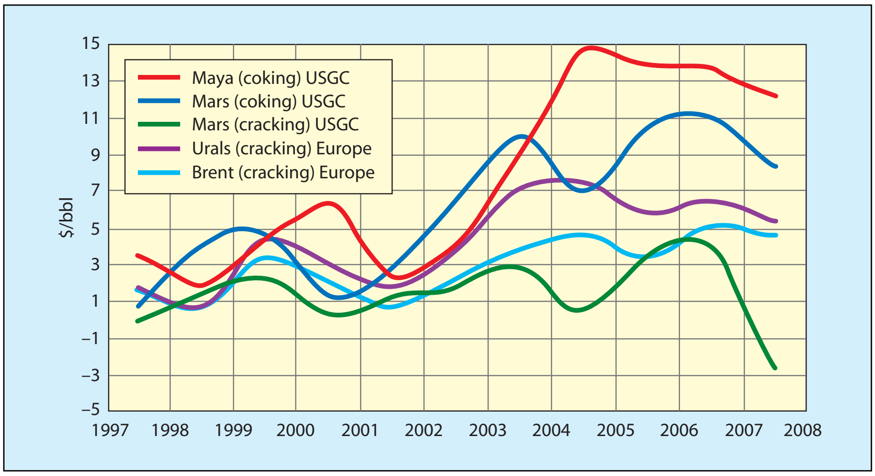

***Figure 1** Past and current cracking and conversion margins. Source: IEA*

FCC in a growing middle distillate market

FCC continues to serve an important role in the refining industry, with an estimated 350–400 FCCUs in operation today. Improvements in technology and catalysis have increased the conversion level of VGO feedstocks into more valuable middle distillates, gasoline and olefin products. Ongoing market changes in pricing and product demands have raised questions over how best FCC assets can be utilised.

While FCC yields vary based on feed quality and process conditions, typical operations yield 50–60 vol% gasoline and 15–20 vol% light cycle oil (LCO) from a VGO feed. Prior to widespread clean fuels introduction, similar pricing for both gasoline and distillate products provided strong incentives for FCC conversion, producing both gasoline and distillate from the low-value fuel oil pool. Continued demand growth for low-sulphur diesel, however, has increased the low sulphur diesel margins, thereby making gasoline production less desirable in some markets.

Globally, both increased coker capacity and increased processing of heavier crudes have resulted in the higher production of lower value, difficult VGOs more suited to the FCC pretreat/FCC complex than a hydrocracking unit due to the high level of feed contamination.

In addition to reviewing how to best optimise FCC operations, Criterion is working with various refiners to increase their middle distillate yield from the FCC pretreat/FCC complex by increasing VGO conversion in the FCC pretreat (PT) unit through modified operating strategies or catalyst systems.

Need for higher activity and stability in pretreatment

Success in the pretreatment of FCC feed is a function of both catalytic performance and catalyst stability. Since being introduced to the market in 2006, Ascent catalysts have been selected globally in over 50 applications involving VGO treatment. Commercial success has been measured by improved FCC operations, longer catalyst cycle lives and the ability to process more difficult feeds. Ascent catalysts are manufactured by a process providing enhanced promoter metals utilisation through an optimised catalyst physical structure designed to better tolerate the contaminant metals present in heavy gas oil feeds.

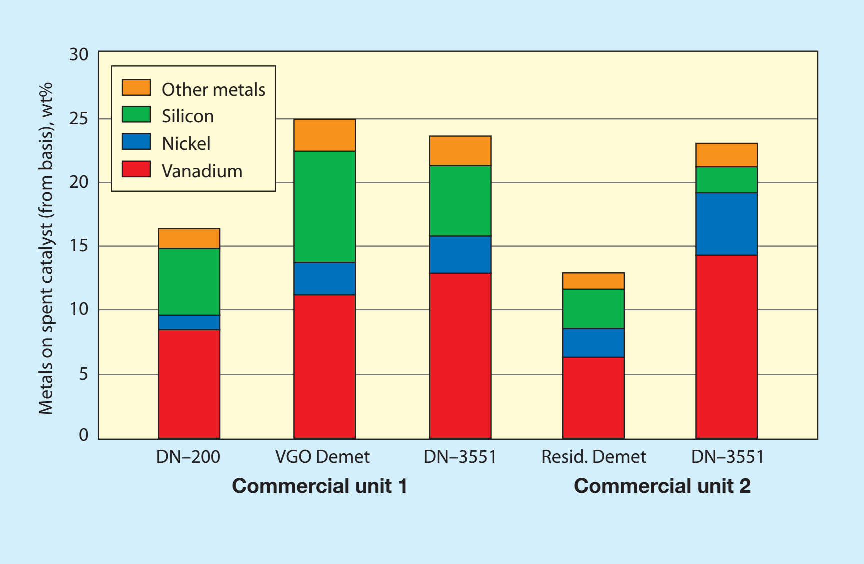

Figure 2 *Improved metals uptake capacity of Ascent DN-3551*

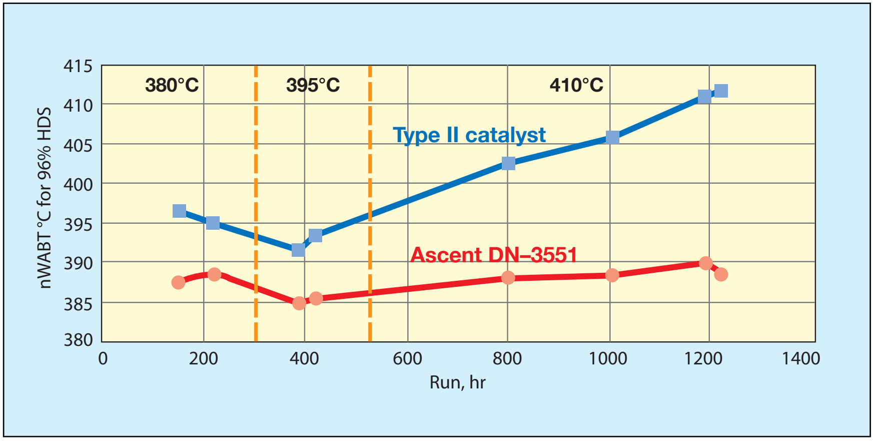

Figure 3 *Accelerated ageing test comparing Ascent stability to Type II catalyst*

Ascent DN-3551 is the most active FCC PT nickel molybdenum (NiMo) catalyst. It is well suited to high-severity FCC PT operations, providing high contaminant metals tolerance while performing a high degree of denitrification (HDN), desulphurisation (HDS) and aromatic saturation (HDA) — reactions critical in FCC feed quality upgrading (to be discussed in more detail in part II of this two-part article). Ascent's DN-3551 NiMo catalyst is designed to achieve very high FCC feed PT to help meet tighter specifications on downstream FCCU operation and product slate (see Case study 2). It can be supplied in an oxide (non-presulphurised) form and provides the advantage of being able to employ conventional handling and start-up procedures and conventional ex-situ regeneration for reuse in the same or lower severity service. The Ascent manufacturing technology produces inherently stronger catalysts that improve recovery during regeneration.

Ascent DC-2551 features similar performance, stability and regenerability to Ascent DN-3551. It is well suited to severe FCC PT operations that value a high desulphurisation performance while reducing the operational hydrogen requirement (to be discussed in more detail in part II). Its design promotes increased HDN and aromatics saturation compared to other cobalt molybdenum (CoMo) catalysts and provides high contaminant metals (nickel, vanadium, silicon) tolerance. Due to its high HDN and aromatic saturation capability, it is able to overcome the FCC conversion loss typically associated with CoMo catalyst application.

Feed and operating conditions

Catalyst system	DN-3551 NiMo
LHSV	0.9 hr-1
Capacity	411 m^3/hr
Pressure	82 bar
H_2/oil	550 m^3/m^3
Feed type	SR GO, SR VGO & 20% HCGO
Feed	
S.G.	0.924
Sulphur, wt%	2.2
Nitrogen, wppm	2400
Concarbon, wt%	0.6
Feed metals, pwwm	<3
D2887 10% - C	332
D2887 95% - C	543
Product GO	
S.G.	0.866
Sulphur, wt%	0.20
Nitrogen, wppm	1200
Concarbon, wt%	<0.3
Feed metals, pwwm	<0.3

Table 1

The use of either of these two catalysts, separately or in a combined system, can be tailored to the FCCU objectives of margin improvement. The FCC PT unit can be operated for targeted desulphurisation, denitrification, maximum polynuclear aromatics (PNA) saturation or to effect some mild hydrocracking.

In addition to high feed contaminant metals tolerance, the Ascent technology produces catalyst with improved tolerance to thermal-based deactivation. This allows for reduced deactivation rates at higher temperatures (see Case studies 1 and 2) and lower hydrogen partial pressures, leading to longer cycle lives in FCC PT units. This improved stability of Ascent catalysts at high temperatures is particularly useful in operations that wish to increase middle distillate production through mild hydrocracking by operating at elevated temperatures (to be discussed in more detail in part II).

Also to be discussed in part II are examples of Ascent catalyst being used to make ULSD and low-sulphur gasoline directly from the FCC PT unit.

Figure 2 shows the improved metal uptake capacity of Ascent catalyst when compared to demetallisation catalysts and the previous generation of FCCU PT catalyst DN-200.

Figure 3 shows the comparative performance in a medium-pressure, accelerated ageing catalyst test of Ascent catalyst vs a Type II catalyst. In this test, the feed and conditions were chosen to accelerate the ageing of the catalyst so that comparative results could be seen in a shorter time.

Case study 1

Extend cycle life in FCC PT unit

Low deactivation rates have been achieved at a refinery that has been operating with Ascent DN-3551 for over one year, following successful runs with previous generations of Criterion catalysts. Processing a challenging mix of crudes and coker feeds, this unit is currently achieving excellent performance with less than half of its previous cycle deactivation rates. The observed superior catalyst activity and stability allow for an extended unit run length, reduce days off stream due to catalyst change-outs and process economically attractive opportunity feeds. Table 1 and Figure 4 give the details of feed operating conditions and performance.

Case study 2

Houston Refining

Employing Ascent systems in its FCC PT helped Lyondell Houston Refining (HRLP), in Houston Texas, to meet the clean fuels challenge successfully and reliably producing Tier II gasoline and ULSD since early 2006. The addition of hydroprocessing capability in FCC naphtha and the expanded capability of the diesel and heavy gas oil hydrotreating units have not only allowed Tier II compliance, but also increased overall facility performance through operational flexibility and yield improvements. To achieve this, a catalyst system is required that has both excellent stability and good performance under varying process conditions.

One particular area of focus is optimisation of the FCC feed hydrotreaters (ie, FCC feed PT) to best manage clean fuels production while maximising FCC performance. Industry-wide, the emphasis of FCC feed hydrotreating has been to provide a constant product sulphur to meet previous gasoline specifications or on the removal of contaminants (nitrogen, polynuclear aromatics (PNA), metals and concarbon) that reduce FCC conversion. Prior to the requirement of 30 ppm sulphur gasoline, FCC feed hydrotreater optimisation resulted in balancing the economics of catalyst cycle life and FCC conversion. The recent change in gasoline sulphur requirements resulted in many refiners, including HRLP, installing post-FCC gasoline hydrotreating technology to meet this mandate. Due to addition of the new post-FCC gasoline hydrotreater, HRLP has shifted away from FCC feed sulphur targets, requiring the refinery to revisit how to best operate the clean fuels system as a whole. This evaluation included accessing the effects of FCC feed hydrotreating severity on FCC conversion and yields as well as its impact on the ULSD hydrotreaters. Awareness and understanding of the interactions between the FCC feed hydrotreaters, the FCCU and the ULSD unit were key to implementing a successful clean fuels strategy.

An important element of hydrotreating improvements at HRLP was significant increases in hydroprocessing performance of the Ascent family of catalysts. Working together with Criterion, HRLP reviewed a number of operational strategies and FCC feed hydrotreater unit technology improvements to better position itself for operation in the future. Currently, HRLP operates two FCC feed units: 634 (Figure 5) and 636 (Figure 6). Key unit parameters are shown in Table 2. Figure 5 illustrates how observed gains in Ascent catalyst activity and stability have increased both units' capability to

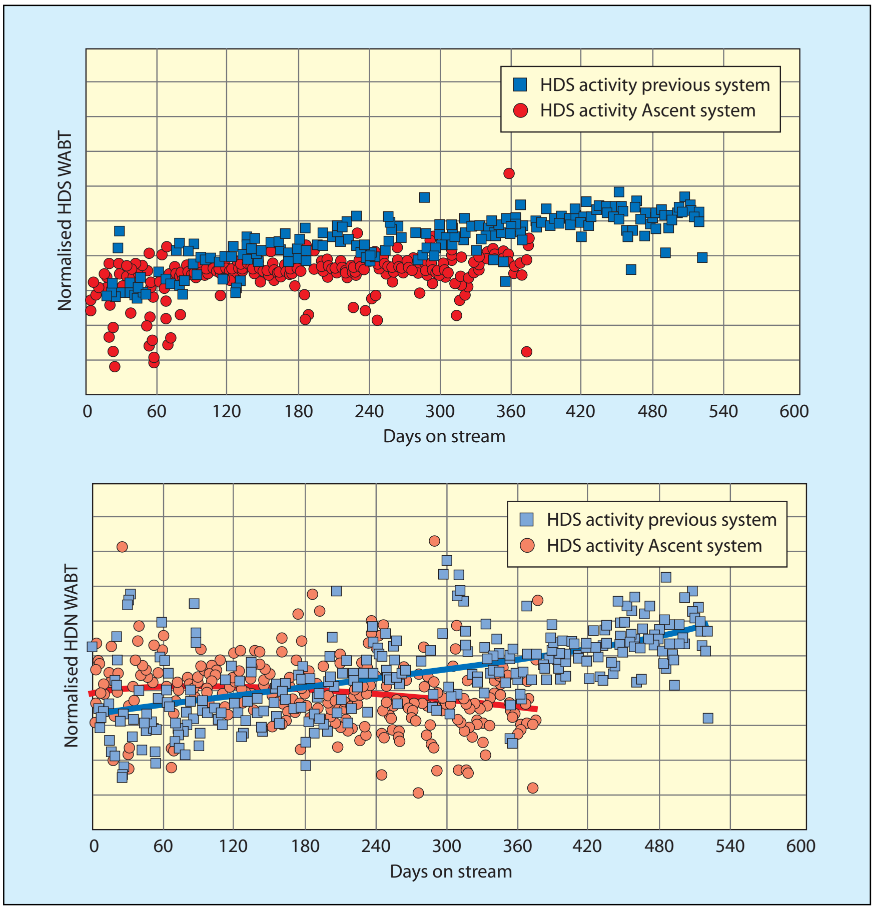

Figure 4 *HDS and HDN stability performance of Ascent catalysts: lower deactivation rates are achieved with DN-3551 compared to previous cycle with an older generation Criterion catalyst, allowing longer cycles*

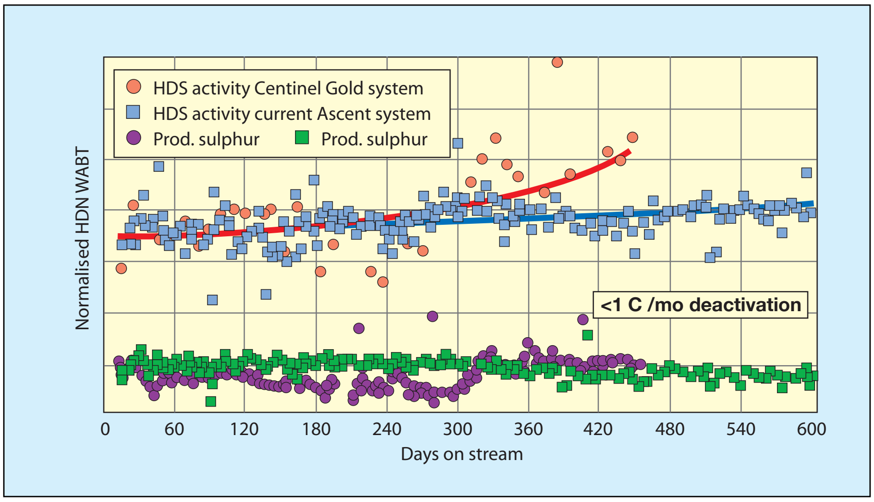

Figure 5 *Stability and activity increase observed in unit 634*

Key unit parameters for the FCC feed hydrotreaters

	Unit 634	Unit 636
LHSV	2.0 hr-1	1.2 hr-1
Pressure	61 bar	95 bar
H_2/oil	185 m^3/m^3	225 m^3/m^3
Feed type	SR VGO SR	VGO & 50% HCGO
Feed		
S.G.	0.935	0.951
Sulphur, wt%	2.0	2.4
D2887 EP% - C	602	593
Hydrogen consumption	76 Nm^3/m^3	110 Nm^3/m^3

Table 2

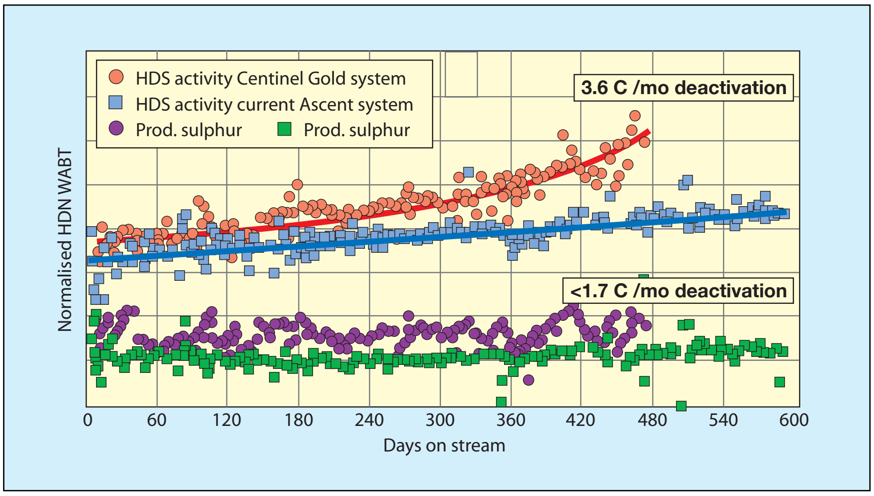

***Figure 6** Stability and activity increase observed in unit 636*

produce improved FCC feed quality while providing longer cycle lengths.

HRLP worked together with Criterion to determine how to take full advantage of the facility's capabilities. Several potential operating modes were examined, including HDS mode, HDN mode, PNA saturation mode and a combination PNA-HDN mode. The cycle length and turnaround cost impact for each mode were considered along with the downstream effects of each mode. Table 3 shows the four operating strategies that were considered along with the characteristics, advantages and disadvantages of each.

The advantages and disadvantages of each of the four operating mode options were considered in an economic analysis. The economic evaluation included amortised catalyst replacement cost and turnaround cost for each mode, as well as FCC conversion shifts for the predicted FCC feed quality in each mode. Given constantly changing market economics and refinery conditions, the economic advantage of one mode over another fluctuates, but HRLP's economic analysis indicated a consistent and significant advantage to run in PNA mode over HDS mode or HDN mode. While PNA-HDN mode is less economically attractive than PNA mode, PNA-HDN mode provides a reasonable compromise between increased FCC conversion and increased FCC feed hydrotreater cycle length. With a plan to operate in PNA mode, PNA-HDN mode is a useful secondary option to allow for some flexibility in turnaround timing. In the second half of 2007, the refinery implemented a plan to run both units 634 and 636 in PNA saturation mode.

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FCC feed hydrotreater operating strategies

Mode	HDS	HDN	PNA	PNA-HDN
Description	Operates throughout cycle to target sulphur removal	Operates throughout cycle to target nitrogen removal	Operates throughout cycle to maximise PNA saturation	Operates for most of cycle to maximise PNA saturation; near the end of cycle, operates to a secondary (nitrogen) limit with lower PNA saturation
Cycle life (for unit 634)	18 months	15 months	10 months	14 months
WABT trend over cycle	Gradual increase over cycle	Gradual increase over cycle	Rapid increase over first 1–2 months, then slow increase throughout cycle	Rapid increase over first 1–2 months, slow increase throughout PNA mode, then rapid increase in HDN mode
Advantages	Longest cycle life, simple to implement	Simple to implement, better FCC feed quality than HDS mode	Best feed quality for FCC conversion, consistent FCC feed quality, achieves high sulphur and nitrogen removal, resulting in improved unit 633 cycle life and/or increased LCO upgrade to ULSD	Longer cycle life than PNA mode, best overall for balancing cycle and FCC feed quality
Disadvantages	Suboptimal FCC feed quality throughout most of cycle, results in lowest FCC conversion, higher LCO yield and higher LCO product (negative impact on unit 633 cycle and/or LCO recovery to ULSD)	Suboptimal FCC feed quality throughout most of cycle, better FCC conversion than HDS mode	Shortest cycle life	Declining FCC feed quality at end of cycle

Table 3