

Resid Fluid Catalytic Cracking (FCC) Catalyst Technology for Maximum Distillates Yield Demonstrated in Big West Oil's Salt Lake City Refinery

Introduction

Recent years have brought a major shift in the world's fuel demand for gasoline and distillate range (diesel) products. While gasoline consumption has shown only minor increases, the demand for distillates has been very strong; mainly driven by the transportation sector. The outlook for the future shows an incremental growth in diesel demand above the 2019 level.

As a result, more and more FCC units are being operated in a maximum diesel mode in order to optimize refining margins. Aside from operational optimizations, such as undercutting gasoline, lower riser temperature, slurry recycling and improvements to hardware, the catalyst has a profound impact on product distribution. If, for example, the activity of the catalyst is adjusted by lowering the riser outlet temperature or by cutting down on catalyst addition, a catalyst not optimized for distillate mode operation could show high residual slurry yields. In the case of resid operations, cutting down on catalyst addition would result in high coke and hydrogen yields, if the catalyst does not feature an optimized metals passivation system.

In order to address customer demands for a highly efficient FCC distillate maximization catalyst technology, BASF dedicated a major R&D program to the development of a new technology platform for FCC catalysts optimized for maximum distillate yield. This platform, known as Proximal Stable Matrix and Zeolite (Prox-SMZ), was first introduced in 2008 with HDXtra[®], a catalyst designed for distillate maximization in Vacuum Gas Oil (VGO) feed FCC units. In 2008 during the first commercial trial of HDXtra in the Frontier El Dorado FCC unit, the data (Table 1) showed a significant increase in distillate yield by 4%, as well as improved bottoms cracking.

As Produced	Base	HDXtra	
Yields, volume %			
Gasoline	56.9	51.5	
LCO	20.7	30.9	+ 10.2%
CSO	5.7	5.1	
Corrected LCO (430-650°F) vol %	16.8	20.8	+ 4%

Table 1: FCC unit yield data of first commercial trial of HDXtra at Frontier, El Dorado, KS

HDUltra®, a distillate maximization co-catalyst that allows for operational flexibility in terms of distillate yield, was launched later in 2009 [2].

In an effort to extend the Prox-SMZ family to resid feed applications with medium to high contaminant metals levels, the novel resid distillate maximization catalyst Stamina® was recently scaled-up from the development stage to commercial manufacturing. This paper describes the development work on Stamina, as well as the first commercial evaluation of the catalyst in the FCC unit of Big West Oil's refinery in Salt Lake City, UT in the second half of 2009.

The Prox-SMZ technology platform

The Prox-SMZ technology is built on two main features: One being the presence of an ultra-stable and coke selective matrix and the other being the close proximity of an ultra-low sodium zeolite and the Prox-SMZ matrix, which are created in one single synthesis step.

Conventionally, low zeolite to matrix surface area ratios (Z/M ratios) are applied to maximize the distillate yield by both increasing the matrix surface area (MSA) and lowering the zeolite surface area (ZSA). However, without further optimization, a lower Z/M ratio results in accentuated matrix cracking with poor coke and gas selectivities. In addition, a matrix with low hydrothermal stability will show favorably low Z/M ratios in the fresh catalysts, but comparably high Z/M ratios in the equilibrium catalyst due to the preferential loss of MSA.

Based on a novel technology, BASF has introduced a unique manufacturing process that yields an advanced matrix material. This matrix material is superior, when compared to conventional matrix materials available to the industry today. The hydrothermal stability of this novel proprietary matrix was compared to a variety of commercially available matrix materials after 1500°F steaming for 4 to 24 hours, as shown in Figure 2. The results show that the novel manufacturing process has resulted in a matrix material demonstrating improved hydrothermal

stability, thereby preserving a good (low) Z/M ratio and high matrix activity even after deactivation. The combination of this matrix with an ultra-low sodium zeolite further improves the overall catalyst stability.

In catalytic testing, conventional high matrix (low Z/M) catalysts were historically known to produce large amounts of coke and dry gas due to rather unselective cracking on matrix surfaces.

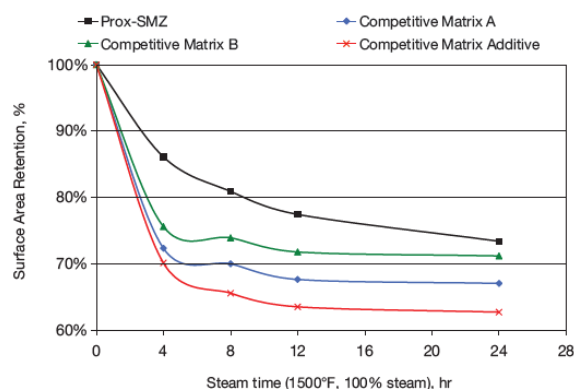


Figure 2: Surface area retention of commercial FCC catalyst matrix materials in comparison to the novel Prox-SMZ matrix.

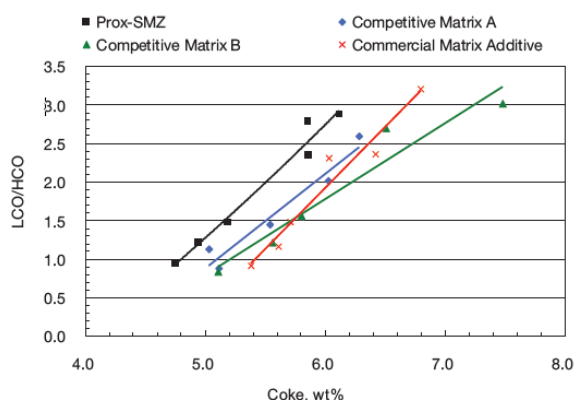


Figure 3: Bottoms upgrading of commercial FCC catalyst matrix materials in comparison to the novel Prox-SMZ matrix.

In order to compare the novel Prox-SMZ matrix to conventional matrix technologies, two typical competitive matrix materials, as well as a matrix additive were tested in a physical blend with RE-USY zeolite (2.6 weight % rare earth oxides). The components were separately steam-deactivated at

1500°F, 4 hours and 100% steam. The blend ratio was adjusted to establish a constant Z/M ratio for all blends. The blends were evaluated for cracking performance in the advanced cracking evaluation (ACE) unit at 970°F with a partially hydrotreated European resid feed with 3.88 weight% concarbon.

The test results in figure 3 clearly showed the advantage of the Prox-SMZ catalyst, featuring a significantly better light cycle oil/ heavy cycle oil (LCO/HCO) or bottoms upgrading ratio at constant coke versus the competitive matrix materials.

The second feature of the Prox-SMZ technology is that it allows for the crystallization of Y zeolite and formation of the Prox-SMZ matrix in a single step. The unique manufacturing process not only forms both the matrix material and zeolite in one single step, but also brings them in intimate contact with one another. The resulting structure is illustrated in an SEM micrograph of the interior of a typical catalyst particle produced in the BASF proprietary manufacturing process (Figure 4). The submicron Y zeolite crystallites are found to be in intimate contact with the Prox-SMZ matrix.

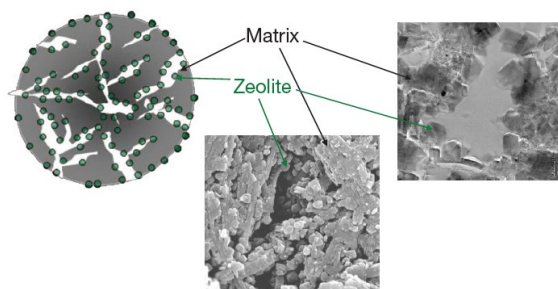


Figure 4: SEM micrographs of a FCC catalyst with Prox-SMZ technology

While other catalyst technologies can incorporate zeolite and matrix materials into the same catalyst particle, they do not have the capability to bring them together in such proximity. The binder used to make these catalysts creates a barrier and will act as a separator between the matrix and zeolite. It is this unique synergy between the zeolite and matrix that leads to rapid transfer of reactant and feed molecules from zeolitic acid sites to matrix acid sites. This enhanced transfer helps to stabilize

coke precursors produced by the matrix cracking, leading to higher LCO production with lower coke.

Development of the Stamina catalyst

After the successful launch of the HDXtra catalyst for distillate maximization in gas oil applications and HDUtra as a distillate maximization co-catalyst, the focus of the R&D work was shifted to the extension of the Prox-SMZ technology to resid applications with high contaminant metals levels. As shown in Figure 5, the goal of the project was to develop a catalyst that matched HDXtra's high distillate yield with the low coke yield of a high quality maximum gasoline resid catalyst, such as BASF's Flex-Tec® DMS technology.

Cornerstones of this R&D work were to create a catalyst that has improved porosity to handle heavier resid feeds and to incorporate metals passivation technologies to minimize the impact of contaminant metals.

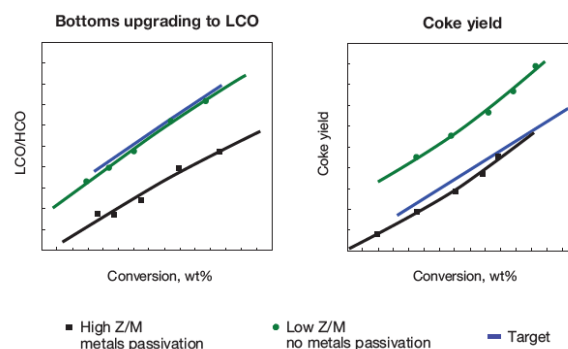


Figure 5: Defining the project objective for the development of Stamina

The newly developed Stamina resid FCC distillate maximization catalyst was scaled-up to manufacturing during the course of 2009.

A catalyst sample obtained from one of the commercial manufacturing trials was tested versus Flex-Tec, BASF's state-of-the-art maximum gasoline resid FCC catalyst. The samples were metallated with 1400 ppm V and 800 ppm Ni and hydrothermally deactivated before testing. As in earlier testing, the catalytic evaluation was performed in an ACE cracking unit at 970°F with a

partially hydrotreated European resid feed with 3.88 weight % concarbon.

As shown in Table 2, the Stamina catalyst showed superior matrix and high zeolite surface area retention, compared to the Flex-Tec reference, which clearly reflects the advantages of the novel Prox-SMZ matrix and the ultra-low sodium zeolite technology.

As Produced Yields, volume %	Flex-Tec	Stamina
Fresh Na ₂ O, wt%	0.20	0.05
Steamed MSA, m ² /g	Base	+ 43
Steamed Z/M	2.7	1.1
ZSA retention, %	Base	+ 6% abs.
MSA retention, %	Base	+ 19% abs.

Table 2: Physical and chemical characterization data for Flex-Tec and a commercially produced Stamina catalyst after steam deactivation (1400 ppm V / 800 ppm Ni)

During catalytic evaluation, Stamina exhibited a 6% improvement in LCO selectivity at 65% conversion over Flex-Tec, while the coke yield stayed constant (Figure 6).

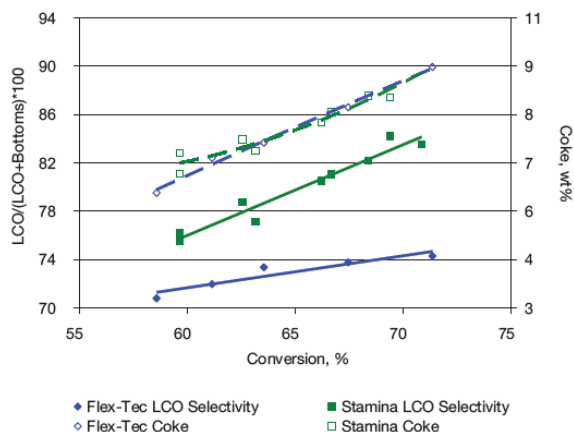


Figure 6: Comparison of the coke yield and the LCO selectivity of Flex-Tec and Stamina

A bottoms reduction of 2% and an increase in naphtha by about 1% at 65% conversion was observed, as shown in Figure 7. The low coke makes at improved bottoms cracking of Stamina is a remarkable result, taking into account that the matrix surface area of the Stamina catalyst was over 40 m²/g or 70% higher, compared to Flex-Tec. The data clearly shows that a true coke selectivity bottoms destruction and LCO maximization is achievable with Stamina.

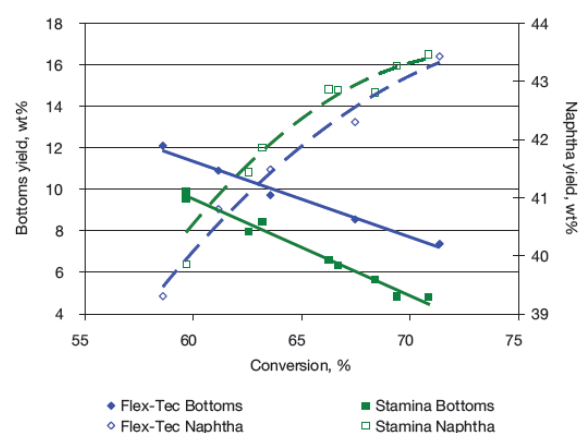


Figure 7: Comparison of the bottoms and the naphtha yield of Flex-Tec and Stamina

Commercial evaluation of Stamina at Big West Oil in Salt Lake City, UT

Following the successful lab testing, Stamina entered the FCC unit of Big West Oil in Salt Lake City in late May of 2009, following Flex-Tec as the previous catalyst grade. The Big West Oil Refinery operates a UOP MSCC resid catalytic cracking unit with the following unit data:

- Reactor Temperature: 965–970°F, Regenerator Bed Temperature: 1335°F
- Unit Capacity: 11,500 BPD; Average feed throughput: 11,000 BPD
- Unit Inventory: 60 tons
- Typical catalyst addition rate: 2.5 tons/day.

The principal unit constraint is the liquefied petroleum gas (LPG) rate, especially during the summer months. The refiner's main objective

during commercial testing was to maximize feed throughput and improve bottoms conversion to LCO and naphtha. There were no major operational or reliability issues during the trial period. The trial period lasted for a total of 160 days. Most independent FCC parameters were kept constant throughout the trial with the exception of a period of low feed rate (1200 bpd or 10% less than normal) during a time span of 30 days in the middle of the trial and reactor temperature higher by several degrees Fahrenheit in the same period. To compare the catalyst performance before and during the trial on a constant basis, the data acquired during the period of lower feed rate is excluded in the following charts. Some changes occurred in terms of feed quality, where smaller fractions of the feed were replaced with lower quality feedstocks (as will be visible from the contaminant metals levels of the equilibrium catalyst).

Soon after the addition of Stamina started, an improvement (drop) in bottoms and a reduction in delta coke could be observed (Figure 8). After completion of the trial, the unit data showed that the delta coke had dropped by 25% and bottoms was 45% lower, compared to the time before the trial.

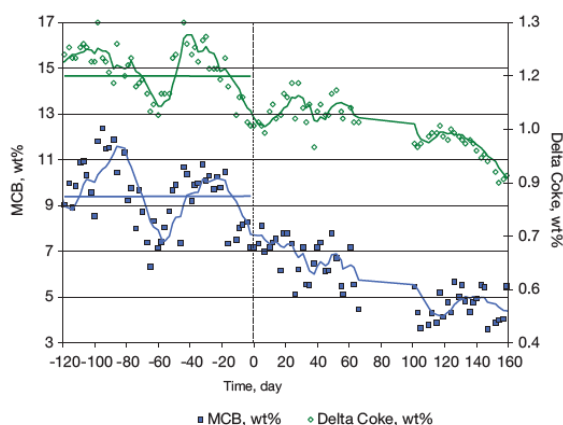


Figure 8: Unit operating data during the trial period, MCB and delta coke

As a result of the improved stability of Stamina and changes in feed quality, the data showed an in

crease conversion, which kept the LCO yield overall flat.

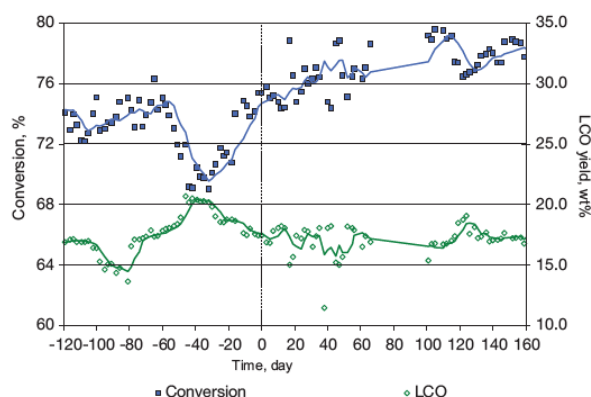


Figure 9: Unit operating data during the trial period, LCO yield and conversion

At the same time, the LCO selectivity improved from 65% to about 80% due to the improvements in bottoms upgrading, while the naphtha yield was 5% higher, compared to the former catalyst (as shown in Figure 10).

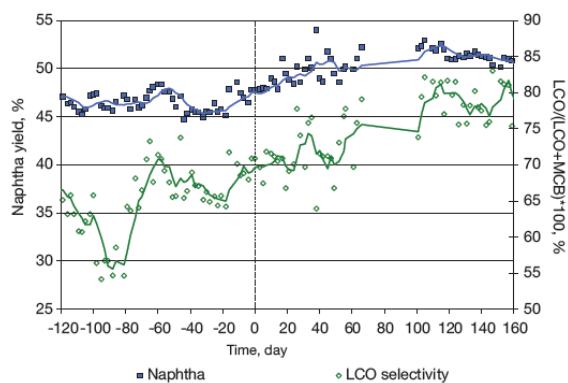


Figure 10: Unit operating data during the trial period, naphtha yield and LCO selectivity

An analysis of the reduced bottoms gravity confirmed the major improvements in bottoms destruction with Stamina (Figure 11).

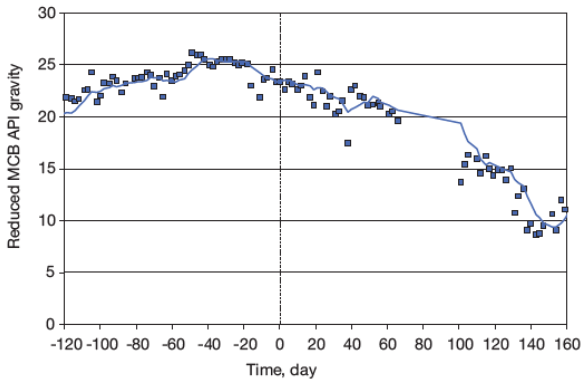


Figure 11: Unit operating data during the trial period, reduced MCB API gravity Ecat lab testing confirms the benefits seen in the unit operation with Stamina

To support the ongoing refinery trial, BASF performed multiple laboratory tests using feed and equilibrium catalyst from the refinery trial to confirm the performance observations at the Big West Oil Refinery. With the start of the trial, a clear increase of the Ecat matrix surface area started, reaching about 90 m²/g versus 40 m²/g before the trial, as shown in Figure 12. As a result, the ZSA/MSA ratio dropped from 2 to 0.8. Despite having a lower fresh zeolite surface area, the ZSA remained flat during the trial, which can be ascribed to the intrinsically higher stability of the ultralow sodium zeolite in Stamina.

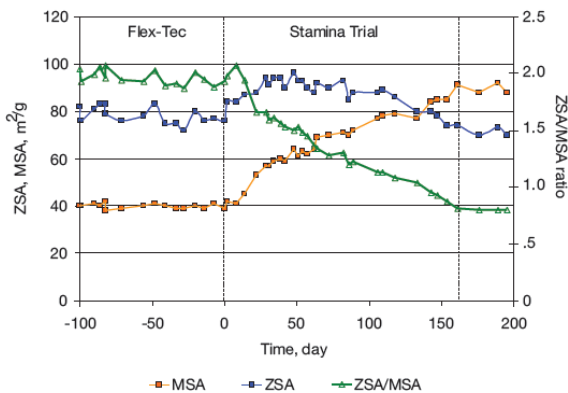


Figure 12: Ecat data before and during the Stamina trial: ZSA, MSA and ZSA/MSA ratio

While the nickel levels on the Ecat remained fairly constant during the trial, a steady increase in iron was observed, reaching values as high as 1.3 wt% (Figure 13).

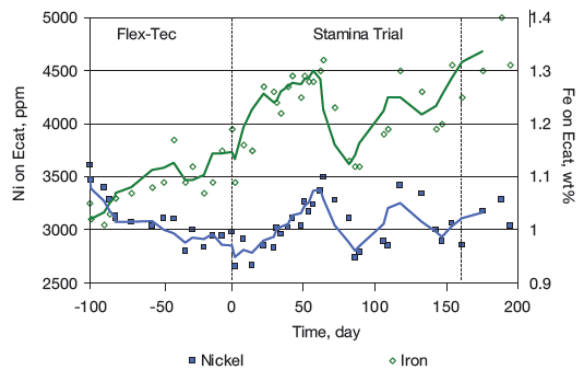


Figure 13: Ecat data before and during the Stamina trial: Nickel and Iron on Ecat

At the same time, periods of high calcium loadings on the Ecat were observed, which are known to lead to rapid catalyst deterioration in combination with high iron levels [3]. As seen in Figure 14, Stamina maintained the activity throughout the period of high calcium and iron concentration as well as during a phase of increased vanadium contamination towards the end of the trial.

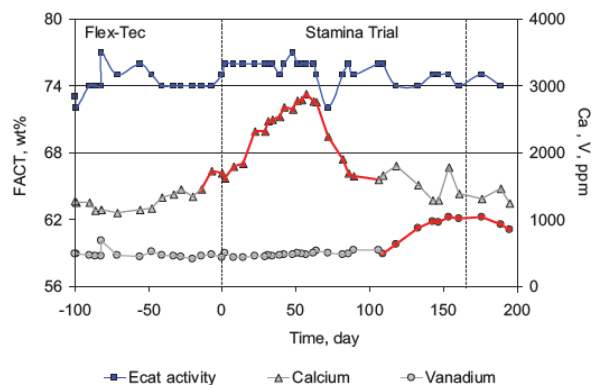


Figure 14: Ecat data before and during the Stamina trial: FACT Ecat activity, Calcium and Vanadium contamination

To follow the change-out during the trial and the change in catalyst performance, catalytic evaluation studies were performed on the ACE unit, using Big West Oil feed and 1000°F reactor temperature. The data of the samples tested as well as the catalytic data are shown below. As mentioned before, the characterization data of the samples that went into the ACE testing study clearly revealed the high stability of the Stamina catalyst's matrix and zeolite. Despite the increase in vanadium at the end of the trial, the data showed a 15% increase in ZSA retention and a 19% increase in matrix surface area retention versus the fresh samples (Table 3).

	Base Flex-Tec	Full change-out to Stamina
Selectivities at constant conversion 70%		
H ₂ (V+Ni corrected), wt%	0.05	0.06
Total C ₂ -, wt%	1.8	1.7
LPG, wt%	18.5	15.7
Naphtha, wt%	42.8	45.9
LCO, wt%	20.7	22.5
Bottoms, wt%	9.3	7.5
Coke, wt%	6.8	6.7

Table 3: Ecat characterization data: Flex-Tec versus Stamina at full change-out

As shown in Table 4, during the course of the trial, the laboratory ACE cracking data showed an improvement (decrease) in bottoms of about 2% at 70% conversion, while LCO increased by about the same amount. At the same time, the naphtha yield was found to be 3% higher versus Flex-Tec, mainly at the expense of LPG.

	Base Flex-Tec	Full change-out to Stamina
Ni, ppm	2981	3000
V, ppm	426	969
Fe, wt%	1.19	1.19
Ca, ppm	1697	1285
Na, wt%	0.46	0.27
MSA Ecat, m ² /g	39	84
Z/M ratio Ecat	1.9	1.0
ZSA retention, %	Base	+ 15
MSA retention, %	Base	+ 19

Table 4: Ecat ACE testing data: Flex-Tec versus Stamina at full change-out



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Technical Note

Modeling results support unit operation data

Based on the run data obtained during the trial, a data reconciliation to constant operating and feed conditions was performed, using the KBC Profimatics® FCC-SIM software. The results are shown in Table 5:

operational effects. These data again confirm the excellent performance of Stamina during this trial.

	Average Flex-Tec Start of Trial	Average Stamina End of Trial	Change	Change % rel.
Product Yields				
Dry gas norm., wt&	2.2	1.8	-0.4	-18,2
Propylene norm, wt%	5.1	5.6	0.5	9.8
C ₄ =norm, wt%	5.2	5.2	0.1	1.7
LPG norm, wt%	17.1	16.4	-0.7	-4.1
Gasoline norm, wt%	46.9	49.3	2.4	5.1
Light Cycle Oil norm, wt%	17.3	20.4	3.1	17.9
SLURRY norm, wt%	9.1	4.3	-4.8	-52.7
Delta Coke	1.13	0.90	-0.2	-20.4
Slurry API gravity	24.1	17.6	-6.5	-27.0

Table 5: Yield reconciliation to constant feed and unit operation conditions

Overall, the modeling results confirm that on the basis of constant operating conditions and feed quality the use of the new Stamina catalyst at Big West Oil led to a reduction in bottoms by almost 5% or over 50% relative and a 20% relative drop in delta coke. Liquid yields increased by over 5% total (3% or 18% relative for LCO and 2.4% or 5% relative for naphtha). The modeling data also suggest that the flat LCO yield seen in the operating data was largely induced by feed and

Profitability

After completion of the trial, Big West Oil performed an assessment of the impact of Stamina on the FCC unit's economics. Overall, the data (Table 6) show major improvements in bottoms and cat gasoline yields, leading to an improvement of 1.56 \$/bbl.

As discussed above, the actual LCO yield was found to be slightly lower on average during the trial period, mainly caused by changes in feed and operating conditions, as confirmed by the Profimatics reconciliation to constant conditions that showed an improvement of LCO.

In addition to the improvements in bottoms and liquid yields, the refinery data show significant improvements in RON (+1) and LPG olefinicity, following a reduction in rare earth on the Stamina catalyst towards the end of the trial.

	Baseline	Trial	Change	Baseline	Trial	Change	Improvement	
	Flex-Tex vol %	Stamina vol %	vol %	Flex-Tec bbl/day	Stamina bbl/day	bbl/day	\$/bbl	\$/d
Cat Gas	56.7%	62.3%	5.6%	5962	6543	590	\$4.22	\$44,284
LCO	17.8%	16.7%	-1.1%	1871	1758	-112	-\$0.79	-\$8,300
Bottoms	9.1%	5.0%	-4.1%	957	523	-434	-\$1.86	-\$19,564
							\$1.56	\$16,420

Table 6: Analysis of Big West Oil's FCC unit economics before and during the Stamina trial (based on 10,500 bbl/d throughput)

Conclusion

The Stamina catalyst trial in Big West Oil's Salt Lake City refinery was successfully concluded in late 2009, showing a reduction in bottoms by over 50% at the benefit of light cycle oil and naphtha, while the delta coke could be improved by 20% relative over the former catalysts. Overall, all the refiner's objectives for the catalyst trial of maximum conversion and bottoms upgrading to LCO and naphtha were fulfilled. As observed earlier for the other members of the Prox-SMZ platform, the novel matrix technology used in Stamina allowed for a significant increase in matrix surface area without negatively impacting the coke yield. The novel Stamina resid distillate maximization catalyst showed extremely high matrix and zeolite surface area stability, even during periods of high iron and calcium contamination. Overall, the refinery reports an improvement in the FCC unit's profitability by more than \$1.5/bbl. Due to the positive outcome of the trial, Big West Oil entered into a regular supply agreement for Stamina at the end of the trial.

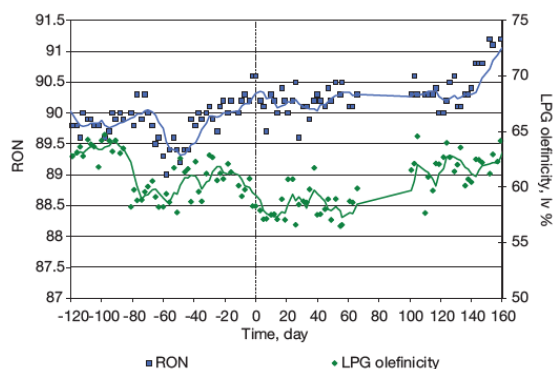


Figure 15: RON and LPG olefinicity, Big West Oil operating data

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