

An Innovative New Technology Platform for FCC Distillate Maximization

Abstract

BASF has developed an innovative catalytic technology platform for maximizing distillate yields from a fluid catalytic cracking (FCC) unit. This unique platform, designated **Prox-SMZ** for **P**roximal **S**table **M**atrix and **Z**eolite, combines attributes from both high zeolite and high matrix activity catalysts. The product is a stable and selective catalyst specifically designed for FCC distillate maximization. Commercial trials demonstrated increased light cycle oil (LCO) yields by up to 5 volume % over baseline catalysts with no reduction in bottoms conversion. The first catalyst from this platform, **HDXtra™**, was commercialized in 2008. Additional products off this platform are being launched in 2009.

Meeting Diesel Demands

With the long-term increase in demand on refiners to process heavier crudes and maximize diesel yields (Figure 1), FCC units will be continually pushed to the edge of their operating limits. Higher diesel yields are often achieved through the use of selective bottoms upgrading FCC catalysts that feature active matrices. However, these conventional bottoms upgrading catalysts increase the yield of undesirable products such as dry gas and coke. This often pushes the FCC unit up against gas compressor or metallurgical limits, not allowing the refiner to take full advantage of the increased diesel yield potential.

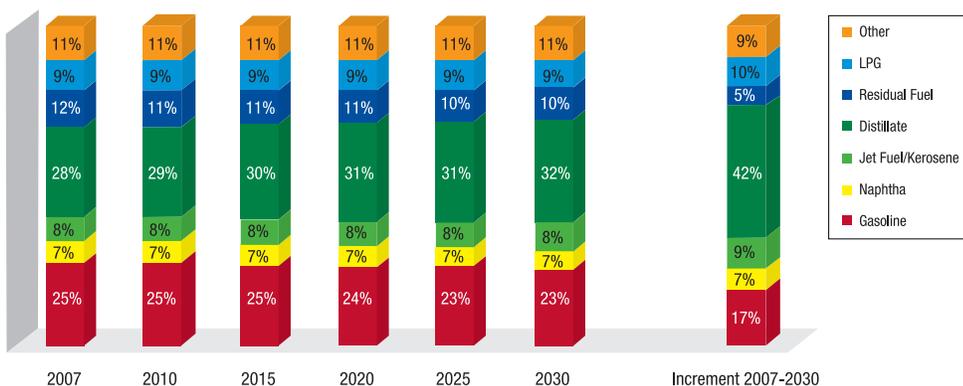


Figure 1: Global refined product demand focused on middle distillates for 2007 – 2030¹.

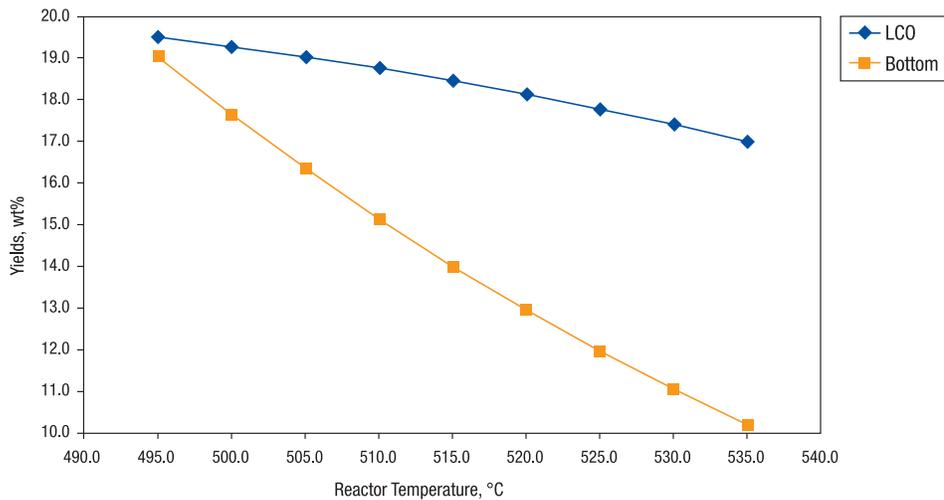


Figure 2: LCO and bottom yields response to decreasing reactor temperature shows that the bottom yield response is more pronounced than LCO.

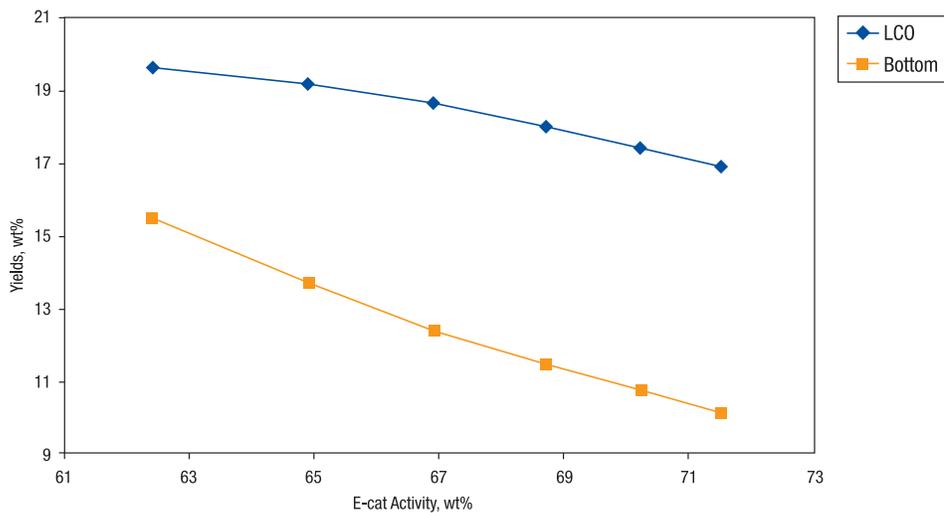


Figure 3: LCO and bottom yields response to lowering the equilibrium catalytic (E-Cat) activity shows that the bottom yield response is more pronounced than LCO.

Distillate Maximization Fundamentals

The fundamental desire within the refining industry would be to convert feed/bottoms in an FCC unit to LCO without further cracking to gasoline. FCC unit operating condition adjustments that can be made include reducing the riser temperatures and/or the catalyst activity by reducing the catalyst make up rate, as shown in Figures 2 and 3. However, both of these options lead to a greater increase in the bottoms yield in comparison to LCO. This clearly is not desirable.

Another approach to increase LCO production is to recycle slurry/bottoms. Second pass yields are typically less selective and lead to higher coke and gas. Use of recycle in an FCC unit constrained by air blower capacity can result in a reduction in feed rate; this can reduce the total production of LCO.

No FCC unit adjustments or combination of adjustments alone will result in increasing LCO without increasing bottoms. Only improvement in catalytic performance offers a pathway to increase LCO production while maintaining bottoms conversion.

BASF Novel Matrix Material

LCO yield can be increased by controlling the depth of cracking. The conventional catalyst approach to increase LCO yield has been to lower the Z/M ratio, typically by both increasing the matrix surface area (MSA) and lowering the zeolite surface area (ZSA).

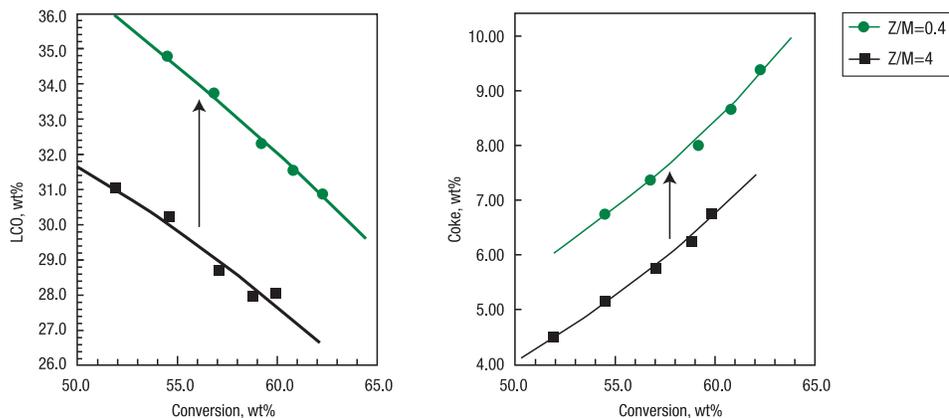


Figure 4a: LCO yield versus conversion; Figure 4b: Coke versus conversion.

However, a lower Z/M ratio results in accentuated matrix cracking with poor coke and gas selectivities. Figures 4a and 4b show a comparison of LCO and coke selectivities for two conventional catalysts at two different Z/M ratios. As previously shown in published literature, lowering Z/M does increase LCO yield but at the expense of coke.

This demonstrates a need for a fundamentally different catalytic approach to increase LCO yield. The need is to have a selective matrix that would increase LCO yield without the accompanying coke yield.

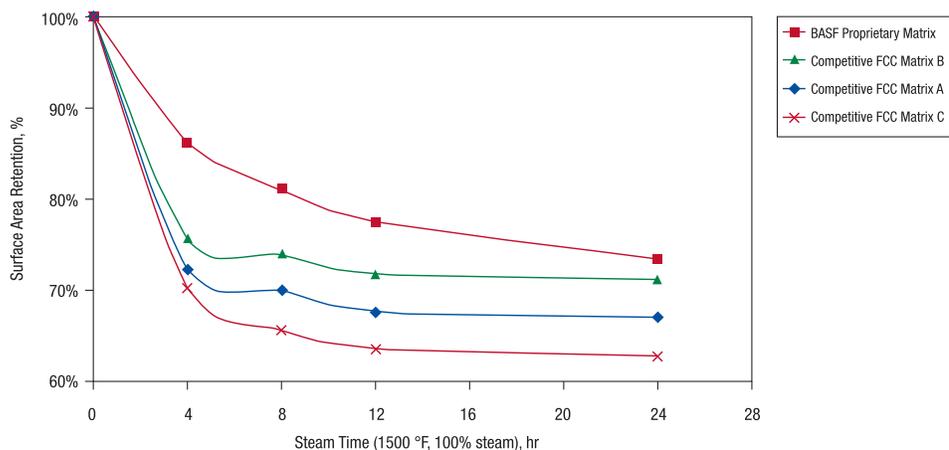


Figure 5: Stability of different matrix materials under hydrothermal conditions.

BASF has introduced a unique manufacturing process that has produced an advanced matrix material. This patented matrix material is based upon a new platform that is different from other conventional matrix materials available to the industry produced by other manufacturing processes. Figure 5 compares the hydrothermal stability of BASF's proprietary matrix with a variety of commercially available matrix materials. It clearly shows that the novel manufacturing process has resulted in a matrix material that demonstrates improved hydrothermal stability.

Most conventional matrix materials, such as alumina, predominantly have Lewis acid sites as measured by pyridine adsorption. This manufacturing process not only generates Lewis acid sites but also a small but significant fraction of Brønsted acid sites (Table 1). The role of Brønsted acid sites in zeolitic cracking is very well known. The Brønsted sites on the matrix material, although weaker than zeolitic sites, are believed to act synergistically with the Lewis sites to enhance the catalytic properties.

	Brønsted acidity (μmol/m ²)	Lewis acidity (μmol/m ²)
BASF novel matrix	0.2	2.51
Matrix A	0	2.59
Matrix B	0	1.57
Matrix C	0	1.81

Table 1: Brønsted and Lewis acidity of different matrix materials.

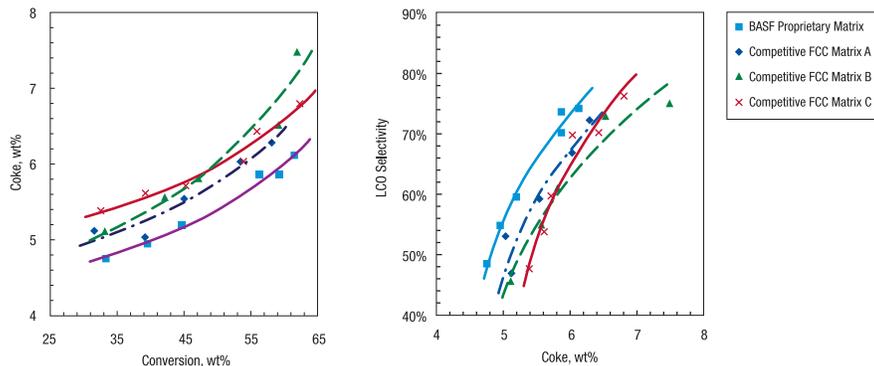


Figure 6a: Coke versus conversion; Figure 6b: LCO selectivity versus coke.

Catalytic properties of the different matrix materials were compared by preparing physical blends of matrix materials with separate particle US-Y zeolite, which had no matrix. Both were separately deactivated at 1500°F, 4 hours and 100% steam. US-Y zeolite had 2.6 weight % rare earth oxides (REO). The blend ratio was adjusted to maintain a constant Z/M ratio. The blends were evaluated for cracking performance in the advanced cracking evaluation (ACE) unit at 970°F with hydrotreated feed containing 3.88 weight % concarbon. LCO selectivity is defined as the ratio of LCO to the sum of LCO and heavy cycle oil (HCO). Three different matrix materials that are used in other FCC catalysts were compared to the new BASF developed matrix material. Figure 6a shows the plot of coke versus conversion for the four different matrix materials tested. The competitive matrix materials had very similar coke yields. In contrast, BASF’s proprietary matrix stood out with lower coke yield. Figure 6b shows a plot of LCO selectivity versus coke yield for the four different blends. The other three matrix materials had similar LCO yields whereas BASF’s proprietary matrix showed higher LCO selectivity.

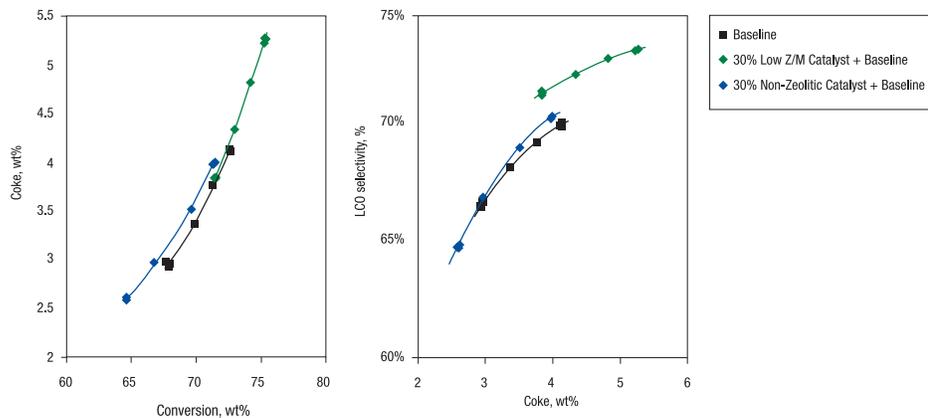


Figure 8a: Coke versus conversion; Figure 8b: LCO selectivity versus coke.

A New Technology Platform

The development of the novel matrix material was extended to include both the crystallization of Y zeolite and formation of the matrix in a single step. The unique manufacturing process not only forms both the matrix material and zeolite in a single step, but also brings them in very intimate contact with an ultra-low Na content. The resulting structure is illustrated in an SEM micrograph (Figure 7) of the interior of a typical catalyst particle. The smaller than 1 μm hexagonal crystallites of Y zeolite are in the immediate vicinity, if not in intimate contact, with the amorphous matrix materials.

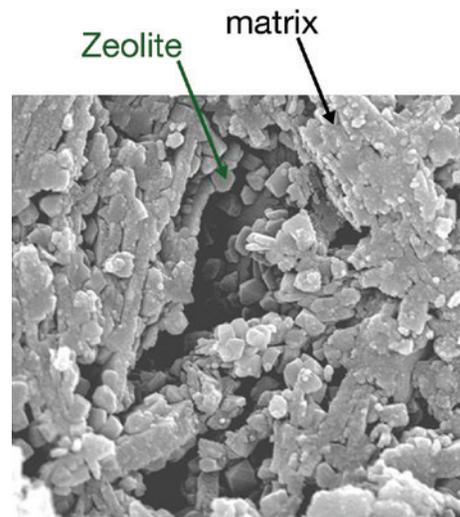


Figure 7: SEM of a BASF FCC catalyst particle from the Prox-SMZ platform.

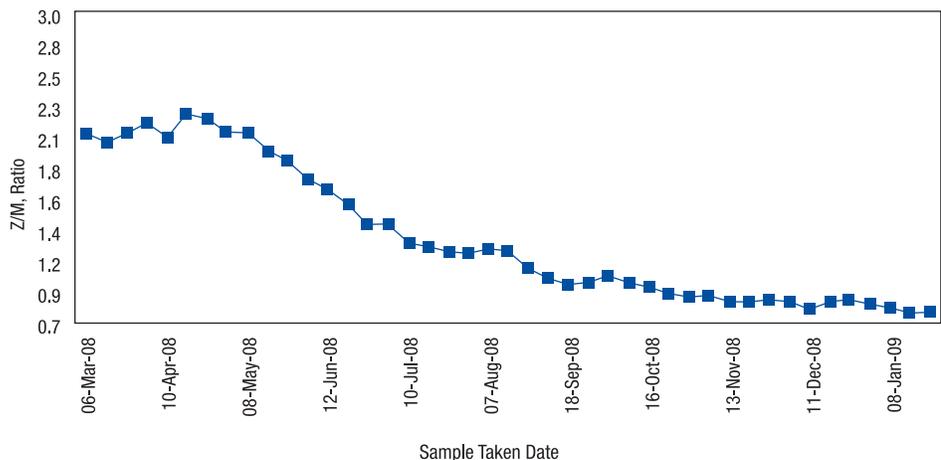


Figure 9: Z/M ratio for HDXtra from the E-cat data at refinery #1.

	Coke at 71 wt% conversion	LCO selectivity at 4 wt% coke
Base	3.76	69.6
Base + 30% Prox-SMZ catalyst	3.82	71.5
Base + 30% competitive matrix only material	4.0	70.2

Table 2: Benefit of Prox-SMZ technology on coke yield and LCO selectivity.

Produced yields, volume %	Base	HDXtra	
Gasoline	56.9	51.5	
LCO	20.7	30.9	← + 10.2%
CSO	5.7	5.1	
Corrected LCO (430 – 650°F)	16.8	20.8	← + 4%

Table 3: Produced yields from refinery #1.

While other catalyst technologies can incorporate zeolite and matrix materials in the same catalyst particle, they do not have the same capability to bring them together in such an intimate contact. It is this unique synergy created by the close proximity of zeolite and matrix that leads to rapid transfer between reactant and feed molecules from zeolitic acid sites to matrix acid sites. The enhanced transfer results in coke precursors produced by matrix cracking being stabilized by zeolite leading to higher LCO production with lower coke.

The benefit of zeolite and matrix synergy was evaluated in a Circulating Riser Unit (CRU) with a mildly hydrotreated gas oil (API gravity = 23.2° and a concarbon of 0.4 weight %). The base catalyst was a Distributed Matrix Structures (DMS) based, high Z/M catalyst targeted for making gasoline. The base catalyst was blended to a 30% level with either the new BASF technology platform catalyst or a commercially available matrix material designed for making LCO. Results are shown in Table 2.

The catalytic performance of the two different blends are compared to the base catalyst in Figure 8a and 8b. The blend containing the new technology platform had lower coke yield and higher LCO selectivity than the blend containing commercially available matrix material.

	Before	After
Feed concarbon, wt%	0.4	1.2
Feed rate, BPD	Base	Base
RXT temp, °F	970	970
Catalyst addition	Base	>15% decrease
Total C3's + C4's, vol %	Base	-1.2
Gasoline, vol %	Base	-3.3
LCO, vol %	Base	+3.3
Bottoms, vol %	Base	+0.4
LCO cetane index	Base	+3
E-cat metals, Ni + V, ppm	220 ppm & 840 ppm V	260 ppm & 1320 ppm V

Table 3: Summary of results from refinery #2.

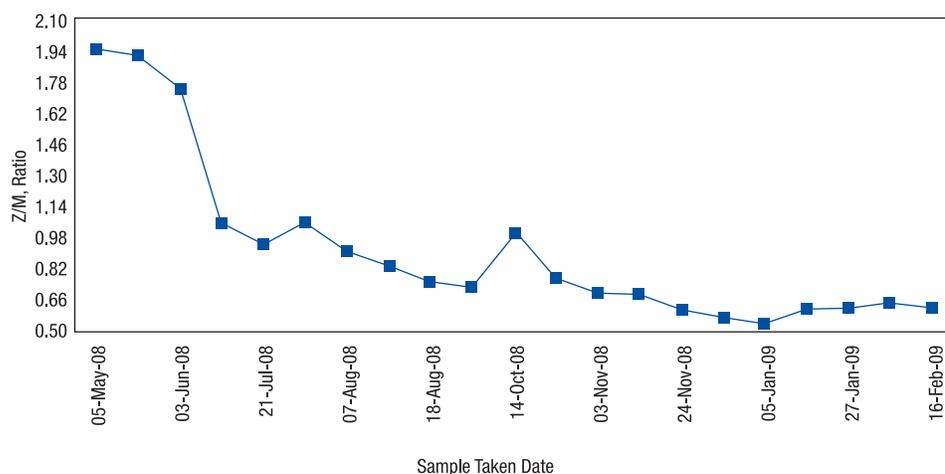


Figure 10a: Z/M ratio for HDXtra from the E-cat data at refinery #2.

This new technology platform is called **Promixal Stable Matrix** and **Zeolite (Prox-SMZ)** and all four of those features play an integral role in the catalytic performance. **Prox-SMZ** is a very flexible platform and can be tailored to individual applications including use with different feeds.

Using the **Prox-SMZ** platform, we have developed and commercialized **HDXtra**, a catalyst specifically targeted for Vacuum Gas Oil (VGO) operations. Other **Prox-SMZ** catalysts, including **Stamina™** for resid feed operations, are currently in the commercialization process.

HDXtra: The Catalyst for LCO Maximization in Vacuum Gas Oil (VGO) Operations

HDXtra is the first commercialized catalyst developed using the **Prox-SMZ** technology platform². This FCC catalyst was specifically engineered for distillate maximization and is targeted for VGO feed operations. Its features include high matrix activity with good coke selectivity, moderate zeolite activity to maximize LCO, and low H-transfer activity to preserve hydrogen in LCO for minimal cetane penalty.

HDXtra has been successfully demonstrated in three commercial trials over the past year.

HDXtra Trial at Refinery #1

The first trial of **HDXtra** was at Frontier in El Dorado, Kansas, USA which operates as a hydrotreated vacuum gas oil refinery. **HDXtra** replaced a **NaphthaMax®II** catalyst. This switch

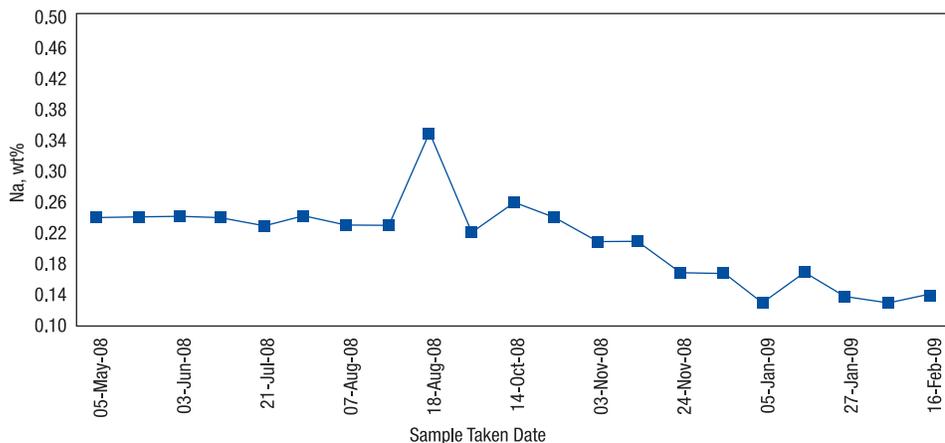


Figure 10b: Na content for HDXtra from the E-cat data at refinery #2.

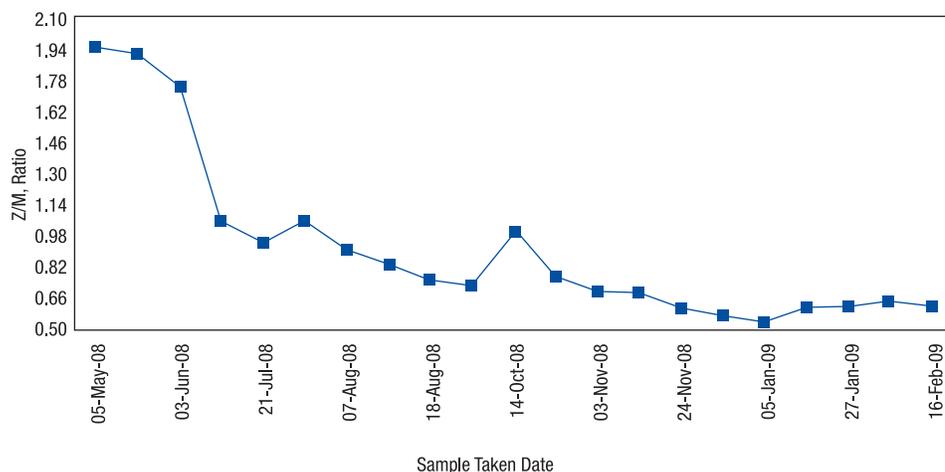


Figure 11a: MSA for HDXtra at refinery #3.

can be most dramatically seen in Figure 9 where E-cat Z/M ratio drops from approximately 2.2 to less than 1. Another noticeable shift was in Na, which on E-cat Na, dropped from 0.22 weight % to below 0.1 weight %.

Highlights of the trial are shown in Table 2. Operating conditions were changed and conversion was dropped from approximately 73 weight % to approximately 64 weight %. At approximately 50 % changeout, an increase in LCO yield of 10.2 weight % was measured. After correcting for conversion, the LCO yield increased by approximately 4 weight %.

HDXtra Trial at Refinery #2

The results from Refinery #2 produced similar results, shown in Table 3.

The LCO volume increases by 3.33 volume % with an increase in the LCO cetane index of 3. Notable reductions in E-cat Z/M and Na are shown in Figures 10a and 10b.

HDXtra Trial at Refinery #3

In Refinery #3, the objectives were to maximize feed rate and maintain gasoline motor octane number (MON). The refinery was previously using a competitive catalyst designed for high LCO yields. The base catalyst already had a relatively high MSA. Switching over from the competitive catalyst to HDXtra increased the MSA from approximately 85 m²/g to roughly 100 m²/g (Figure 11a). As in previous trials E-cat Na dropped dramatically during

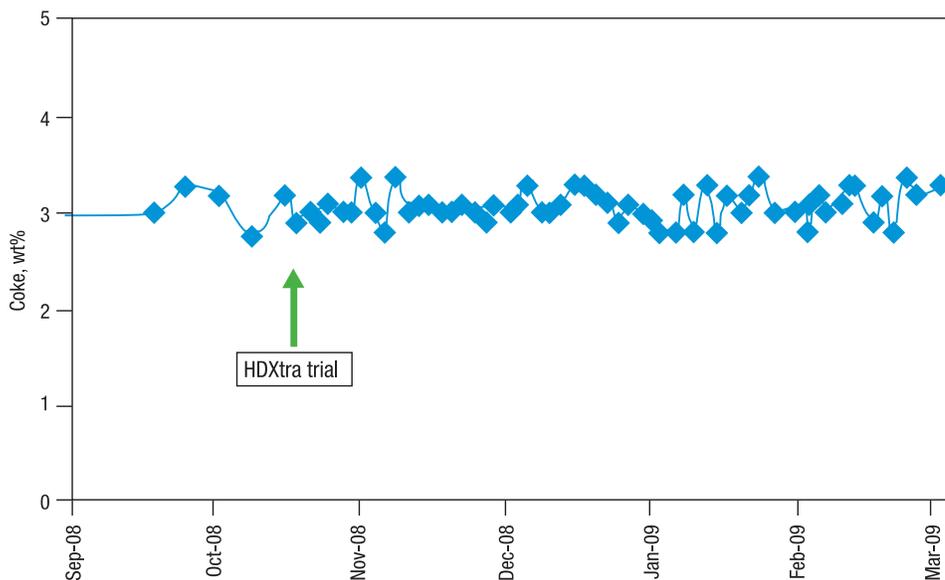


Figure 11b: ACE coke levels of HDXtra over time at refinery #3.

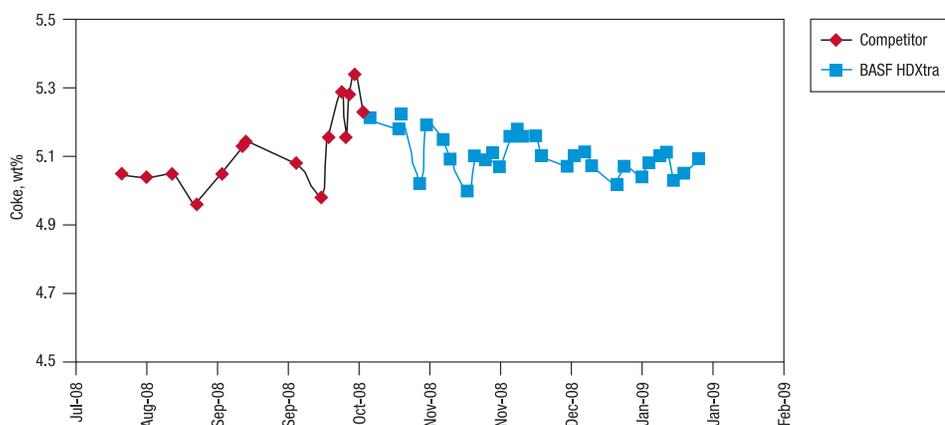


Figure 11c: FCC unit coke levels of HDXtra compared with the competitor at refinery #3.

the trial from approximately 0.25 weight % Na to less than 0.1 weight %. This decrease in Na not only improves the stability of zeolite and the matrix, but also decreases the hydride transfer, which positively impacts cetane.

Although the MSA increased, it did not detrimentally impact the coke yield (Figure 11a). This reinforces the experimental observation during product development that not all matrices are equal in their catalytic behavior. In Refinery #3, the ACE coke and FCC unit coke data remained at the same levels, as seen in Figures 11b and 11c. Unlike traditional high MSA catalysts, **HDXtra** did not lead to coke penalties, which shows that all MSA are not equal.

Further observations of E-cat changeover at Refinery #3 shows how **HDXtra** has the lowest commercially available Na (Figure 11d).

Refinery #3's normalized diesel production operating data shows that the FCC reached unprecedented maximum levels (Figure 11e) while slurry yield remained (Figure 11f) constant.

Table 4 shows an almost 2 weight % increase in LCO at Refinery #3 when using **HDXtra** over the base catalyst.

HDXtra Refinery Trials Conclusion

BASF's E-cat benchmarking database has shown that relative to competitive offerings, **HDXtra** trials have some of the highest MSA and matrix stability available as shown in Figure 12a and the

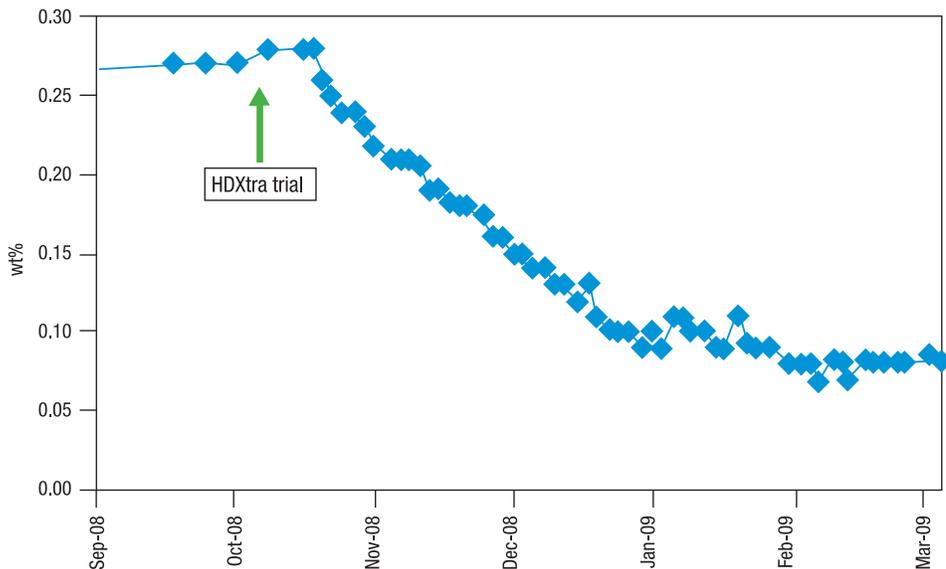


Figure 11d: Na levels over time at refinery #3.

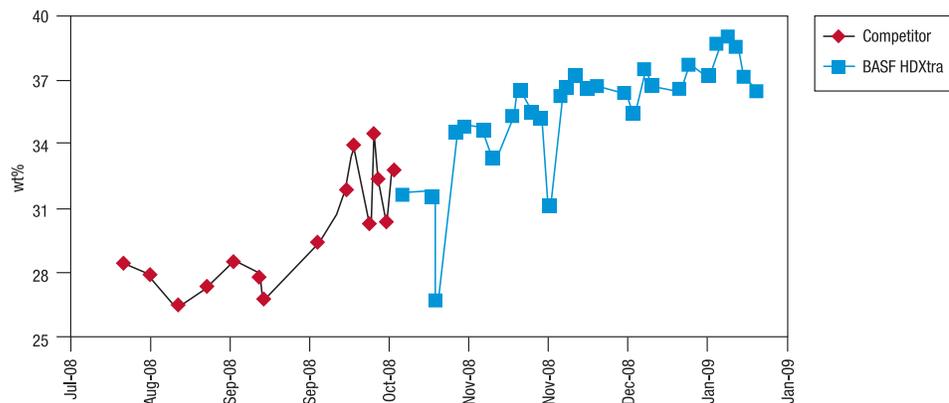


Figure 11e: Normalized LCO and HCN levels at refinery #3.

lowest Na content, as shown in Figure 12b. Both factors result in higher gasoline octane and better LCO cetane in the unit. All three trials show a significant increase in normalized LCO yield while the coke and slurry levels remain constant. ACE testing of E-cats confirmed the results. **HDXtra catalyst, BASF's first product derived from the proprietary Prox-SMZ technology platform**, sets a new standard in the industry for delivering the best FCC refining economics when running for LCO maximization with hydrotreated feeds.

Moving Forward

With **HDXtra** already on the market, BASF is designing an entire set of solutions based on the new **Prox-SMZ** technology platform to address the needs of the refining industry. **Stamina**, an FCC catalyst for distillate maximization targeted for resid feed operations, is currently undergoing extensive internal manufacturing trials. This catalyst was designed with more macroporosity for heavy molecule access as well as the addition of proven metals tolerance features.

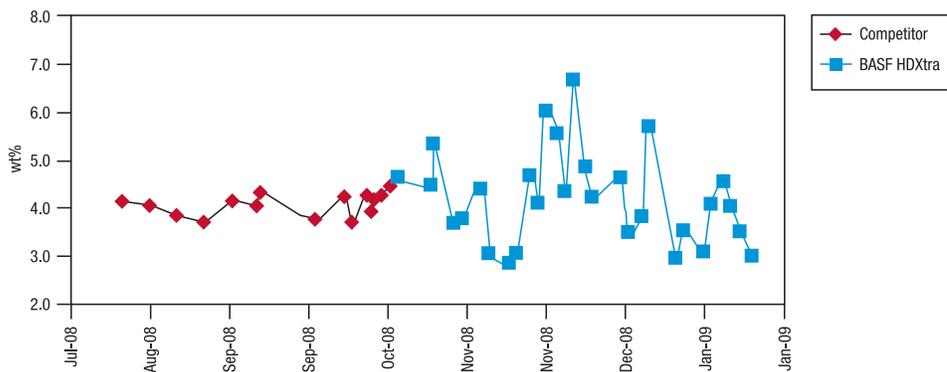


Figure 11f: Normalized slurry levels at refinery #3.

CASES CORRECTED FOR CUT POINT, FEED RATE, FEED QUALITY AND OP. CONDITIONS

Catalyst Supplier		Competitor	BASF	Δ
Case Title		Base Case	HDXtra	
Case Date		October '08	January '09	
Conversion				
- Corrected Fresh Feed Conversion	wt%	76.10	74.47	-1.63
Product Yields				
Weight Percent Basis				
- H2+C1+C2+C2=	wt%	2.12	2.05	-0.07
- Total C3 + C4	wt%	22.38	19.69	-2.69
- Corrected C5+ Gasoline	wt%	46.50	47.73	1.23
- Corrected Light Cycle Oil	wt%	21.78	23.60	1.82
- Corrected SLURRY	wt%	2.12	1.93	-0.19
- Coke	wt%	5.09	5.00	-0.09
Product Properties				
- Gasoline RON	RON	92.5	93.2	0.7
- Gasoline MON	MON	80.4	80.6	0.1

Table 4: Customer operating data at refinery #3.

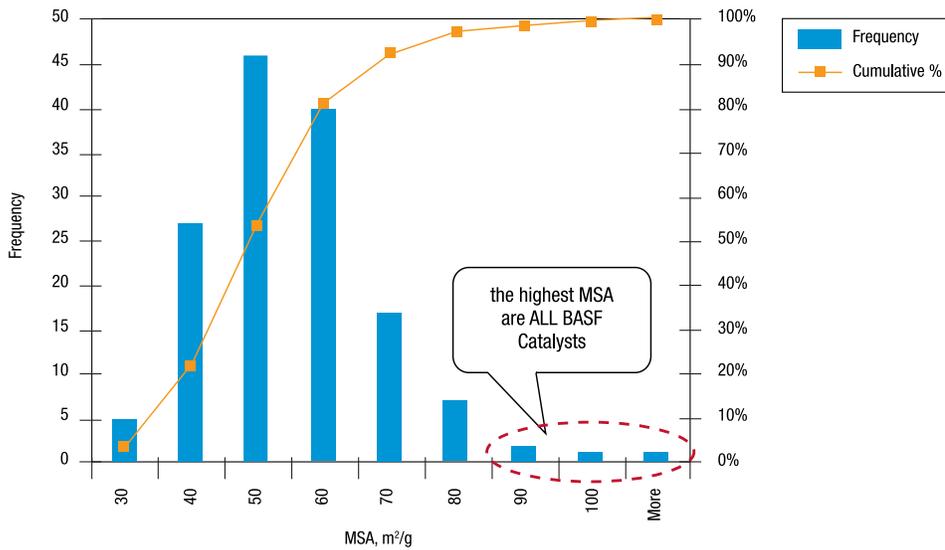


Figure 12a : Histogram showing MSA from all BASF benchmark data.

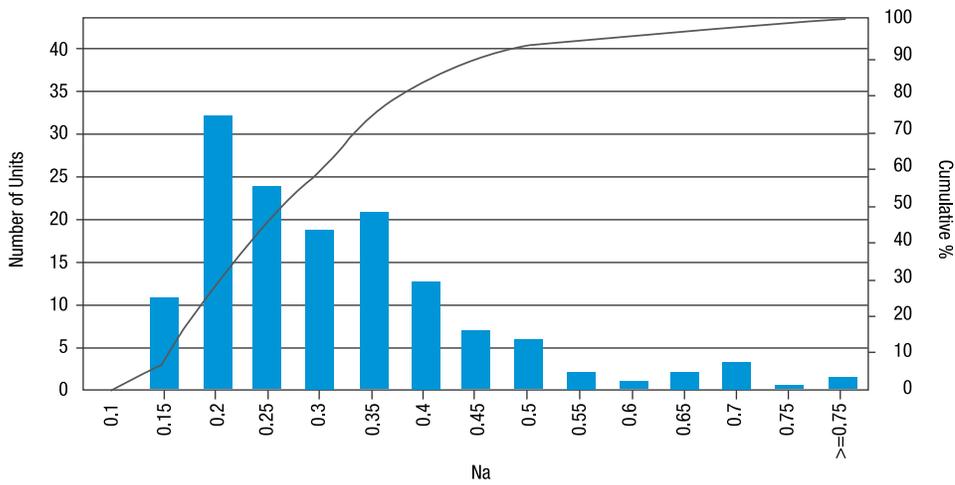


Figure 12b: Histogram showing the Na content from all BASF benchmark data.

References

1. Hart's World Refining and Fuels Service (WRFS) 2009.
2. McLean, J. B., "The Role of FCC Catalyst Technology in Maximizing Diesel Production – Two North American Refinery Success Stories." 2009 NPRA paper.

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