Jointly Developed FCC Catalysts with Novel Mesoporous Zeolite Deliver Higher Yields and Economic Value to Refiners

Background

Rive Technology and Grace Davison are commercializing advanced fluid catalytic cracking (FCC) catalyst technology that dramatically increases the yield of transportation fuels per barrel of crude oil. Rive’s Molecular Highway™ technology makes traditional zeolite catalysts more capable of cracking large hydrocarbon molecules, and allows valuable primary cracked products, like gasoline and diesel molecules, to more readily escape the catalyst before they are overcracked to less valuable light gases and coke. This new catalyst is a drop-in replacement for current catalysts and will enable refiners to increase throughput and profitability without capital investment. In this paper we explain Rive™ zeolite technology, describe its incorporation into a Grace proprietary catalyst matrix formulation, and discuss preparations for a first refinery trial later this spring.
Rive’s Molecular Highway™ Technology

Since the introduction of zeolite-based catalytic cracking in the 1960’s, zeolite Y has been the active ingredient of choice. It’s relatively stable at the high temperatures within the FCC unit (up to about 1400˚F) and very efficient at catalyzing the cracking of smaller FCC feed molecules that can enter through its micropores, (with pore mouths of about 0.7 nm.). However, as illustrated in Figure 1, many feed molecules are too large to enter Y zeolite micropores and must first pre-crack less selectively either thermally or outside of the zeolite before entering the zeolite crystals. Similarly, larger gasoline and LCO product molecules are a tight fit within zeolite pores and can take a relatively long time to leave the zeolite crystal. During that relatively long stay within the micropores, such valuable products can be recracked (overcracked) to less valuable gases and coke.

Rive™ zeolite technology was invented at MIT in the early 2000’s by Garcia-Martinez and Ying. It improves on zeolite Y by creating a network of intermediate sized (2 - 6 nm.) mesoporous “molecular highways” throughout the crystals of zeolite Y. These “molecular highways” admit and pre-crack even the largest feed molecules, while also channeling product gasoline and diesel molecules safely out of the zeolite.

Mesopores in Rive™ zeolite can be clearly seen in transmission electron microscope (TEM) images, such as those shown in Figure 2. Figure 2a is a TEM image of a conventional Y zeolite crystal showing its rows of lattice reflection lines resulting from the regular atomic structure within the crystal (a few are highlighted in red for clarity). Figure 2b of a mesoporous Rive™ zeolite crystal similarly shows the crystal lattice lines, but in addition one can see the larger, lighter colored spots corresponding to the mesopores in the Rive™ zeolite (a few of which are circled in red).

The size and volume of mesopores created in Y zeolite can be controlled over a fairly wide range with Rive’s Molecular Highway™ technology. Figure 3, below, shows a pore size distribution typical of that used for catalytic cracking. The graph compares the cumulative pore volumes of both Rive™ Y zeolite and conventional Y zeolite as a function of pore diameter, and it shows that both types contain a large volume of micropores at <20 Å. (<2 nm.) diameter. In addition, however, Rive™
Figure 2a
TEM Photomicrograph of Standard Y Zeolite

Figure 2b
TEM Photomicrograph of Mesoporous Rive™ Y Zeolite

Figure 3
Argon Adsorption Showing 40 Angstrom Mesopores Created in Y Zeolite by Rive’s Molecular Highway™ Technology
zeolite also contains about 0.15 cc/gm of larger pores in a very narrow range at about 40 Å in size. These 40 Å (4 nm), "meso" sized pores are unique to Rive™ zeolite and are the key to achieving the superior cracking yields described below. The catalytic impact of these zeolite mesopores complements matrix porosity that has been fine-tuned by FCC catalyst manufacturers over the past 50 years of zeolite based FCC catalysts.

Catalytic Properties of Rive™ Zeolites and Catalysts

Initial screening experiments for catalytic cracking of VGO were done by Dr. Garcia-Martinez to compare the cracking yields of powdered pure mesoporous ultrastable Y zeolite (USY) with pure conventional USY in a fluid bed micro-activity test unit at the National Center for Upgrading Technology (NCUT) in Devon, Alberta, Canada, and the results showed greatly improved yields with the mesoporous material.

Figure 4, shows a yield comparison of zeolites steamed for 4 hours at 1450°F and 100% steam. At equal 70 wt.% conversion, mesoporous USY increased gasoline yield 10% relative from 42% to 47%, increased distillate (LCO) yield by 20% relative, and decreased coke yield by 20% relative! These selectivity improvements were a dramatic confirmation of the benefits of zeolite mesoporosity for improving large-molecule cracking and reducing loss of gasoline to coke and gases.

Since that time Rive Technology has focused its efforts on capturing that magnitude of improved performance (i.e., uplift) in formulated FCC catalysts. In mid-2010 Rive and Grace Davison entered a joint development and marketing agreement for products that combine Rive’s Molecular Highway™ technology with Grace’s market leading knowledge of catalyst formulation and manufacturing. The program’s goal is to develop revolutionary new FCC catalysts based on the two technologies. Progress has been rapid, and a first refinery trial is planned for late spring of 2011.

Initial work focused on formulations using relatively inert silica sol matrices with testing being done at the Chemical Processing Engineering Research Institute (CPERI), Thessaloniki, Greece. A range of formulations was tested, and Figure 5, below,
shows ACE testing results for a preferred formulation after steaming for 4 hrs at 1450°F and 100% steam.

Table I lists the feed properties. While the feed used for this study had a relatively low CCR and 90% boiling point, its low API gravity and high Ca show that it is relatively aromatic and difficult to crack.

Figure 5a is a plot of gasoline yield vs. conversion comparing a catalyst containing Rive™ zeolite (in Red) to a catalyst containing conventional zeolite. The zeolites were processed to have the same steamed crystal unit cell size and the catalysts had the same zeolite contents and matrix formulations.

Figure 5a shows that the benefits of Rive™ zeolite mesoporosity translate well from pure zeolite powders to catalysts. In this case the uplift was about 3 percentage points (about 6% relative) compared to the catalyst made using conventional zeolite.

<table>
<thead>
<tr>
<th>Table I</th>
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<td>CPERI Feedstock Properties</td>
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<tr>
<td>°API</td>
<td>19.60</td>
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<tr>
<td>CCR</td>
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<tr>
<td>Sulfur</td>
<td>2.39%</td>
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<tr>
<td>IBP</td>
<td>577°F</td>
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<tr>
<td>50%</td>
<td>831°F</td>
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<tr>
<td>95%</td>
<td>1000°F</td>
</tr>
<tr>
<td>Kwatson</td>
<td>11.63</td>
</tr>
<tr>
<td>Ca</td>
<td>25.75</td>
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</table>
Similarly, Figure 5b compares the coke yields of the two catalysts and shows that the catalyst having Rive™ zeolite made about 1 percentage point (15% relative) less coke than the catalyst containing conventional zeolite.

LCO yields (Figure 5c) were similar for the two catalysts, though, so the advantage in bottoms cracking seen with the pure powders was diminished when mesoporous zeolite was formulated into a silica sol matrix and used to crack this relatively challenging feedstock.

The first commercial catalyst formulations containing Rive™ mesoporous zeolite were developed based on ACE testing using paraffinic vacuum gasoil. Controls for these tests were alumina-matrix commercial catalysts A (moderate
rare earth) and B (high rare earth). Both equilibrium catalyst and lab deactivated fresh catalysts were used in the comparisons.

Figure 6 contains graphs of conversion vs. cat/oil ratio, and selectivities vs. conversion for the equilibrium and lab deactivated versions of commercial catalyst A. It shows that the deactivation conditions used for this test (8 hrs/1450°F/100% steam) were somewhat less severe than that experienced in the FCCU, but the selectivity matches were excellent.

Figure 7, below, is a comparison of a steamed GRX™ catalyst formulation containing a moderate rare earth mesoporous Rive™ zeolite with lab steamed commercial catalyst A. The two catalysts were substantially equal in activity, yielding similar conversions at equal cat/oil ratios. There was also little difference in gasoline selectivity between the two. There was, however, a significant benefit in bottoms upgrading and coke selectivity for the GRX™ catalyst containing mesoporous Rive™ zeolite, and those benefits are particularly evident in the graph of bottoms.
yield vs. coke. At constant 3% coke, the GRX™ catalyst produced 1/3 lower bottoms relative to the catalyst containing conventional zeolite (5% vs. nearly 8%).

Figure 8 below shows a similar comparison for GRX™ and conventional zeolite-containing alumina matrix catalysts at higher rare earth content. Again catalyst activities were equal, but at higher rare earth level there was a significant gasoline yield advantage for the GRX™ catalyst with mesoporous Rive™ zeolite, along with improved bottoms cracking and coke selectivity.

Overall, Rive™ mesoporous zeolites in different catalyst formulations tested to-date have consistently showed selectivity benefits in one form or another in all tests. The degree of benefit has varied depending upon the overall formulation, and the feedstock used for the test, but directionally performance benefits in bottoms upgrading, gasoline yield, coke selectivity and/or olefinicity have consistently been demonstrated.

Catalyst formulation work is continuing with the objective of achieving the level of selectivity improvement seen with pure zeolite powders. As of today, comparing the catalytic results achieved with pure powdered zeolites with those from formulated catalysts, we estimate that these excellent first improvements have the potential to double when the full potential of the technology is realized.

**Figure 7**
Alumina Matrix Catalyst Formulation Containing Mesoporous Rive™ Zeolite Matched the Activity and Had Improved Selectivity vs. a Commercial Alumina Matrix Catalyst Containing Conventional Zeolite (at Equal, Moderate, ReO)
**Economic Value – Creating $0.79 per Barrel in the Refinery**

Because of the complex inter-relationship between different units in a refinery and with economic factors like crude pricing and the value spread between feed and cracked products, it is challenging to relate catalyst performance to refinery value. Rive Technology has used industry-standard AspenTech PIMS and KBC Profimatics modeling tools to bridge the gap between lab test results and economic value to the refiner.

The analytical process is shown in Figure 9, below. ACE testing data measured at either CPERI or Grace Davison is processed using either Profimatics FCC-SIMTM process simulation software, or a proprietary kinetic model developed by Rive Technology to produce catalyst performance factors that, in turn, are converted to Profimatics catalyst factors. Shift vectors generated with Profimatics are then input to a PIMS model of a standard reference refinery and the operation is optimized. Sensitivity analyses have been run on variables such as crude or product pricing, the value spread between feedstocks and products, and different operating limits.
To ensure that crude costs and refinery product pricing data are input into the PIMS model in a consistent manner, correlations were developed based on historic data. We found that the historic cost of each crude and the price for each refinery product could be predicted well using linear functions of the prevailing 3–2–1 Crack Spread and the cost of West Texas Intermediate crude (WTI). Therefore, for any projected WTI cost and crack spread, the price of each crude and each product could be setup systematically in the model.

The hypothetical reference refinery for this process has a 150,000 bpd crude capacity with a 42,000 bpd FCC unit. It has both sour and sweet crude stills. Refinery constraints are listed below:

1. Sweet crude is at rate limit (sour crude rate is usually not a limit, but can be set if desired)
2. Naphtha hydrotreater is feed limited (i.e. reformer naphtha feed treater)
3. FCC is coke limited
4. Hydrocracker is at rate limit
5. Coker is at rate limit
6. Product blending specs

Catalyst factors and shift vectors for the example analysis are based on the GRX/Commercial catalyst comparison summarized in Figure 7. Crude price is set at $75/bbl of West Texas Intermediate (WTI) based on the 2 year average spot price March 2009 thru February 2011. The crack spread is assumed to be $10/bbl; which is consistent with long range projections from the Energy Information Administration (EIA). Later we will show the impact of changes in crude price and crack spread on the economics.

Table II show the PIMS estimates for 2 operating cases. In Case 1 crude rates were allowed to float within the unit constraints of the reference refinery. In Case 2 crude rates were constrained to the levels optimized for the base catalyst case.

Case 1 shows that increased economic value results from the following factors:

1. The combination of improved coke selectivity and reduced gas selectivity for the GRX catalyst with Rive™ mesoporous zeolite allows both the quality of the feed to the FCC unit to be reduced and reactor top temperature to be increased 17°F while keeping within the FCCU coke limit.
   a. Coker Distillate is rerouted from the FCC to the distillate hydrotreater, which augments and improves diesel blending stock and makes the FCCU feed heavier.
   b. Sweet crude train is limited, but to make up diverted FCCU feed and to provide more blend stock for higher quality products coming from the FCCU, more sour crude is run. Naphtha cut point is decreased to
stay within the reformer naphtha pretreater feed limit, thereby swinging more material to kero (jet).
c. FCCU feed rate decreases 1.8%, and feed quality is reduced.
d. Increased riser top temperature results in increased FCCU conversion and also increases the octane and olefin content of the cracked products. Negative value bottoms fall 15%.
2. Feed to the alkylation unit increases as a result of greater olefins from the FCCU and together with the increased octane from the FCCU, total octane barrels is sustained.
3. Added jet from crude allows more FCC hydrotreated heavy naphtha to be blended into diesel instead of jet.
4. Hydrocracker is at its maximum feedrate, but the unit is able to shift yields to more naphtha and less distillate due to increased diesel from both FCC hydrotreated heavy naphtha and coker distillate.
5. Reformer pretreater is limited, but 2.1%

Table II
Incremental Value of Improved Catalytic Selectivity from GRX™ FCC Catalyst
All data shown are relative to base case (not shown)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1: Optimized Crude Rates</th>
<th>Case 2: Crude Rates Constrained to Base Case</th>
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<tbody>
<tr>
<td>Refinery Throughput</td>
<td>+5.3 vol.%</td>
<td>NA</td>
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<tr>
<td><strong>Refinery Profitability</strong></td>
<td><strong>+0.79 $/bbl crude</strong></td>
<td><strong>+0.47 $/bbl crude</strong></td>
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<tr>
<td>Refinery Products:</td>
<td></td>
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<tr>
<td>LPG</td>
<td>+0.3 vol.% of crude</td>
<td>+0.2 vol.% of crude</td>
</tr>
<tr>
<td>Gas</td>
<td>+1.0 vol.% of crude</td>
<td>+0.3 vol.% of crude</td>
</tr>
<tr>
<td>Distillates</td>
<td>+3.8 vol.% of crude</td>
<td>+2.7 vol.% of crude</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>+0.3 vol.% of crude</td>
<td>-2.6 vol.% of crude</td>
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<tr>
<td>FCC Riser Temperature</td>
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<td>+11˚F</td>
</tr>
<tr>
<td>FCC Rate</td>
<td>-1.8 vol.% of crude</td>
<td>-2.0 vol.% of crude</td>
</tr>
<tr>
<td><strong>FCC Yields:</strong></td>
<td></td>
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<tr>
<td>Conversion</td>
<td>+3.8 wt.%</td>
<td>+4.4 wt.%</td>
</tr>
<tr>
<td>Gas</td>
<td>+0.6 wt.%</td>
<td>+0.6 wt.%</td>
</tr>
<tr>
<td>C₃+ C₄ Olefins</td>
<td>+1.2 wt.%</td>
<td>+1.2 wt.%</td>
</tr>
<tr>
<td>C₃+ C₄ Non-Olefins</td>
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<td>+1.7 wt.%</td>
</tr>
<tr>
<td>Gasoline</td>
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<td>+0.8 wt.%</td>
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<td>Distillate</td>
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<td>-2.4 wt.%</td>
</tr>
<tr>
<td>Bottoms</td>
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<td>-2.0 wt.%</td>
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<tr>
<td>Coke (constant max coke rate constraint)</td>
<td>+0.2 wt.%</td>
<td>+0.1 wt.%</td>
</tr>
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</table>
more reformate is produced due to more Hydrocracker naphtha production (which does not need to go through the constrained pretreater).

The net result of these changes, shown in Table II, is a 5.3% increase in refinery throughput with 1.0% coming in gasoline and 3.8% in distillates. The net value of these improvements is $0.79/bbl ($118,000/day, or $43,000,000/yr).

Case 2 in Table II focuses on the value to the FCCU alone by constraining the refinery feed rate to base case levels. Consequently the spillover value to other units is diminished, but there is still an increase in overall distillate and gasoline yields of 3.0% of the crude rate, and the FCCU experiences a 2 wt% drop in bottoms yield. Increased gasoline octane and olefins yields also help sustain octane-barrels.

The values in Table II are based upon a crude price of $75/bbl and a crack spread of $10/bbl. Figure 10, below, shows the impact of changes to these values on the increased profitability of Case 1. It plots the value uplift in $/bbl of crude vs.

Figure 10
Improved Profitability from FCC Catalyst Containing Rive™ Mesoporous Zeolite as a Function of Crude Cost and Crack Spread

The graph shows that value uplift due to the improved selectivity of GRX™ catalyst containing mesoporous Rive™ zeolite increases nearly linearly with crack spread and roughly the same with increases in crude price. It is highly profitable in all combinations within the explored range. Even under the least favorable condition of $63/bbl crude price and $5/bbl crack spread, the uplift is worth $0.52/bbl crude (ca. $28,000,000/yr). At the most favorable conditions the value uplift is $1.04/bbl crude, or ca. $57,000,000/yr. While it is not shown, sensitivity analysis also indicates that the value uplift due to improved FCC catalyst selectivity is approximately linear with refinery size.
Commercialization

Manufacturing of the first FCC catalyst from this joint program between Grace Davison and Rive Technology is now moving from the pilot scale to full commercial production. Thousands of pounds of Rive™ Y zeolite have been produced at the pilot plant of Grace’s Curtis Bay, MD manufacturing facility, and, as you can see from Figure 11, below, its performance matches that of smaller scale materials made in Rive's Princeton NJ laboratory. Figure 11 compares two catalysts made using the same formulation and rare earth level, but one catalyst contained Rive™ zeolite that was processed in the laboratory and the other contained Rive™ zeolite that was produced in the pilot plant.

Figure 11 shows that catalyst made with pilot plant Rive™ zeolite was more active and had equal selectivity compared to catalyst made using lab-produced Rive™ zeolite. Continuous calcination at the tech center allowed for more uniform stabilization of the zeolite which, in turn, produced a more crystalline and more hydrothermally stable product. At equal zeolite content the pilot plant catalyst had a steamed zeolite surface area of 190 m²/gm compared to 160 m²/gm for the catalyst with lab produced zeolite. Consequently, the pilot plant catalyst had about 25% higher activity (i.e., pilot plant zeolite catalyst achieved 75% conversion at 5.5 cat/oil vs. 7 cat/oil for the lab catalyst).

Figure 11 Scale-up of Rive™ Zeolite Manufacturing Process at the Grace Davison Technical Center Produced Excellent Quality
Otherwise, the two catalysts were identical. Figure 10 shows that there were no differences in either the gasoline, LCO, or coke selectivities of the two catalysts.

Based on these excellent results, plant modifications to accommodate the Rive process are in progress, and a first refinery trial is scheduled for later in the spring of 2011.

What's Next?

Along with FCC catalysts based upon Y zeolite, Rive and Grace Davison plan to introduce mesoporous ZSM-5 based catalysts and additives for cracking. Laboratory progress is well along on these materials, and, if things go as expected, first results should be ready for publication by late this year or early in 2012.

References

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