"Increasing Butylenes Production from the FCC Unit through Rive's Molecular Highway™ Technology"

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Abstract:

In preparation for the Tier 3 standards going into effect in the United States in 2017, refiners are striving to find ways to reduce the sulfur content of their gasoline pool. Refiners have a limited number of options to reduce gasoline sulfur levels to meet the new 10 ppm requirement. For Tier 2 compliance, some refiners opted to install equipment for gasoline post-hydrotreating, which led to some octane loss. For Tier 3, removing the remaining, more difficult sulfur molecules may lead to more significant octane loss. Accordingly, alkylate has emerged as a preferred gasoline blending component, as it contains no sulfur, no olefins, no benzene and has a low vapor pressure and high octane number. Unfortunately, many refiners struggle to maximize their alkylate production due to a shortage of butylenes.

Rive Technology (Rive) has developed and commercialized Molecular Highway™ technology whereby a precise series of mesopores are engineered into Y zeolite, the primary active component of all FCC catalysts. These mesopores significantly improve diffusion of FCC feed molecules into and out of the zeolite crystals of the FCC catalyst. Prior AFPM papers have focused on the value created by Molecular Highway™ technology through improved coke selectivity, enhanced bottoms upgrading, and decreased dry gas production.

Commercial trials across multiple refineries have also demonstrated Rive's capability to increase butylenes production for a given set of operating conditions. These valuable, reactive molecules are quickly and efficiently channeled through the mesopores of the zeolite instead of succumbing to secondary and tertiary cracking reactions, which would turn them into butane and dry gas. In addition, many refiners in the United States utilize ZSM-5 additives to convert gasoline-range olefins to LPG olefins. Because Rive also preserves the olefinicity of the gasoline-range molecules, the combined system of Rive FCC catalyst with ZSM-5 additives has shown dramatic increases in butylenes yield.

This paper will further investigate Rive's Molecular Highway™ technology and discuss how it can be applied to increase butylenes production in the FCC unit, allowing refiners to better respond to Tier 3 standards.

Background:

Under the final Tier 3 program starting January 1st, 2017, for most U.S. refiners, gasoline will be required to meet an annual average of 10 ppm sulfur[1]. While the program includes a number of alternatives such as credit averaging, banking, and trading, refiners have a limited number of operational options to meet this goal.

The Fluid Catalytic Cracking (FCC) unit produces about one half of the refinery's gasoline pool volume but typically contributes around three quarters of the total sulfur, so it clearly becomes a key focal point for sulfur compliance. A review of FCC unit options to reduce gasoline sulfur yields the following possibilities:

- Purchase sweeter FCC feed
- Increase the degree of Cat Feed Hydrotreating
- Reduce the gasoline end point
- Post-(hydro)-treat the FCC gasoline
- Utilize gasoline sulfur reduction FCC additives
- Increase the yield of butylenes for additional alkylation

While these are all viable options, most will increase daily operating expenses, and some could require capital investment. For Tier 2, many refiners opted to install equipment for gasoline post-hydrotreating. This approach often led to octane loss. For Tier 3 compliance, removing the remaining sulfur molecules, which are the most difficult to hydrotreat, may lead to a much larger octane loss.

Accordingly, alkylation is one of the more cost-attractive solutions. Alkylate is a preferred gasoline blending component due to its valuable properties; however, many refiners struggle to maximize their alkylate production due to a shortage of butylenes.

Rive's Molecular Highway^{TM} Technology:

Rive and W.R Grace continue to jointly develop and commercialize Molecular Highway^{TM} technology for use in FCC units throughout North America. The "Rive" process introduces a vast network of intermediate-sized (~40 Angstrom) mesopores into the zeolite, which significantly enhances diffusion of the feed and cracked products through the catalyst.

In Figure 1, the picture on the left shows a photomicrograph of conventional Y zeolite. Each crystal face contains millions of 7.5 Angstrom diameter micropores, which are too small to see even at the 100,000x magnification. The picture on the right shows a photomicrograph of Rive's zeolite. While the micropores still cannot be seen at this magnification, the extensive network of Rive's mesopores are clearly viewable.

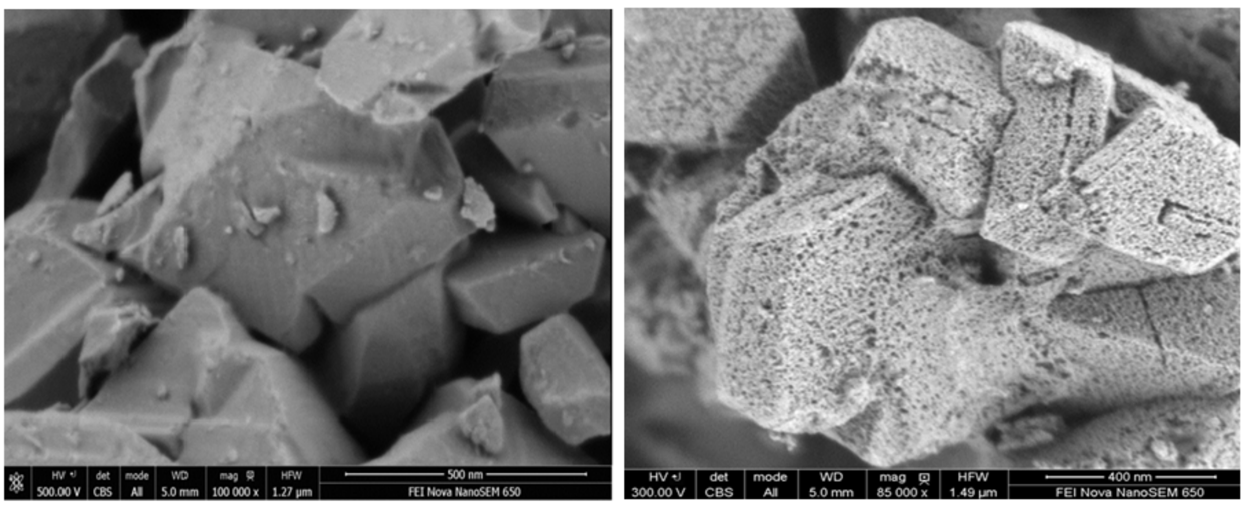

Figure 1: Photomicrographs of Conventional Zeolite (left) and Rive Zeolite (right)

Importantly, the mesopores shown above in the Rive zeolites are homogeneously distributed and interconnected within the zeolite. Professor Zou and her team at Stockholm University recently used their cutting edge imaging techniques to investigate the internal architecture of Rive's zeolite. Electron tomography and rotational electron diffraction were utilized to provide an unprecedented look inside the zeolite crystal, as shown in Figure 2. The images show clear evidence that Rive's mesopores are homogeneously distributed and interconnected within the zeolite, enabling enhanced diffusion of molecules into and out of the zeolite, thereby improving catalytic performance[2].

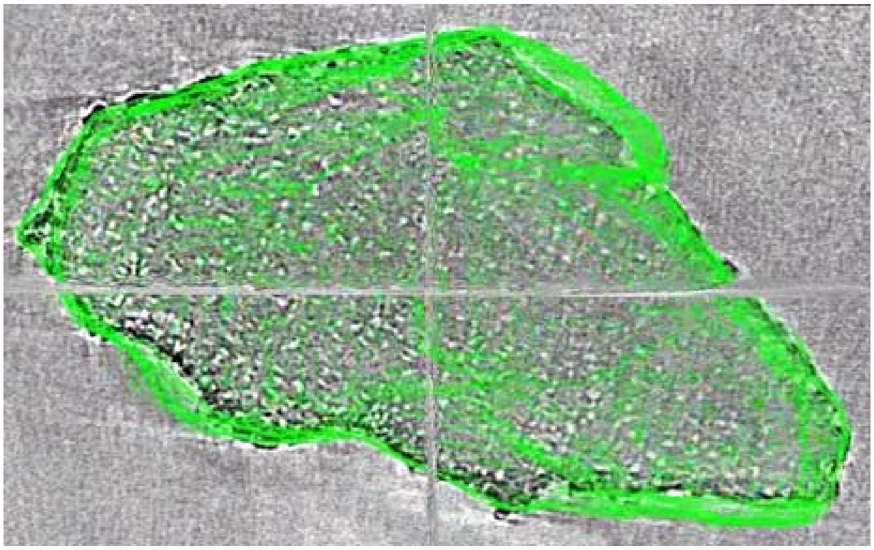

Figure 2: Molecular Highways in Rive zeolite

As a result of Rive's interconnected network of mesopores, larger feed molecules which boil at temperatures above 950°F are able to access the zeolite. The strong acid sites in the zeolite are able to crack the larger feed molecules much more selectively than conventional active matrix materials. Additionally, these Molecular Highways rapidly channel the valuable cracked products out of the zeolite before they succumb to potentially undesirable reactions such as thermal cracking, hydrogen transfer, or condensation reactions. These concepts are illustrated below in Figure 3.

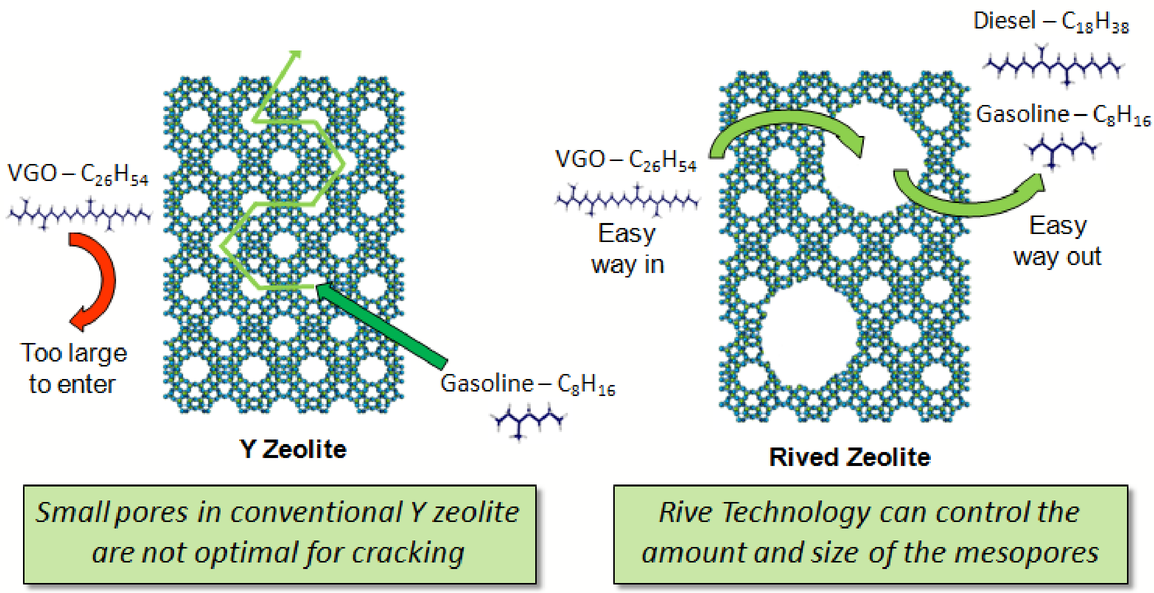

Figure 3: Overview of Rive's Molecular Highway™ Technology

Typical benefits from Rive's catalyst include improved bottoms upgrading, decreased delta coke, and decreased dry gas production. Rive has used these trademark benefits to increase FCC feed throughput by alleviating existing unit constraints such as maximum Air Blower rate, Wet Gas Compressor rate, and Regenerator temperature. Two of Rive's commercial trials – CountryMark Refining and Alon USA – have been well-documented in previous AFPM papers (AM-12-25 and AM-13-03, respectively) and have provided excellent uplift to the refiners.

Another benefit provided by Rive catalyst is increased LPG olefinicity. Butylenes are especially important to U.S. refineries in order to maximize production of low-sulfur, high-octane blending alkylate.

LPG olefins such as propylene and butylene are very reactive, particularly at high temperatures such as those present within the FCC Riser and Reactor. If these valuable, reactive molecules spend too much time inside the catalyst, they can become saturated through hydrogen transfer reactions into less-valuable LPG paraffins, thermally crack into methane and ethane, or condense within the catalyst pores to form coke. Rive's intermediate-size mesopores have been proven to allow rapid transport of valuable LPG olefins out of the zeolite.

For refiners operating against a wet gas constraint, Rive Technology offers the ability to optimize the unit for constant LPG yield with higher olefinicity.

<u>Laboratory Testing</u>:

An independent R&D facility recently performed ACE testing across two FCC catalyst formulations. These formulations were identical, with the only exception being that one catalyst contained conventional zeolite, while the other catalyst contained Rive's zeolite.

As shown in Figure 4, there was a noticeable increase in C_4 olefinicity with the Rive catalyst. At 75% conversion, the Rive catalyst formulation showed a relative boost in C_4 olefinicity of approximately 3% compared to the conventional catalyst, without increasing the total LPG yield.

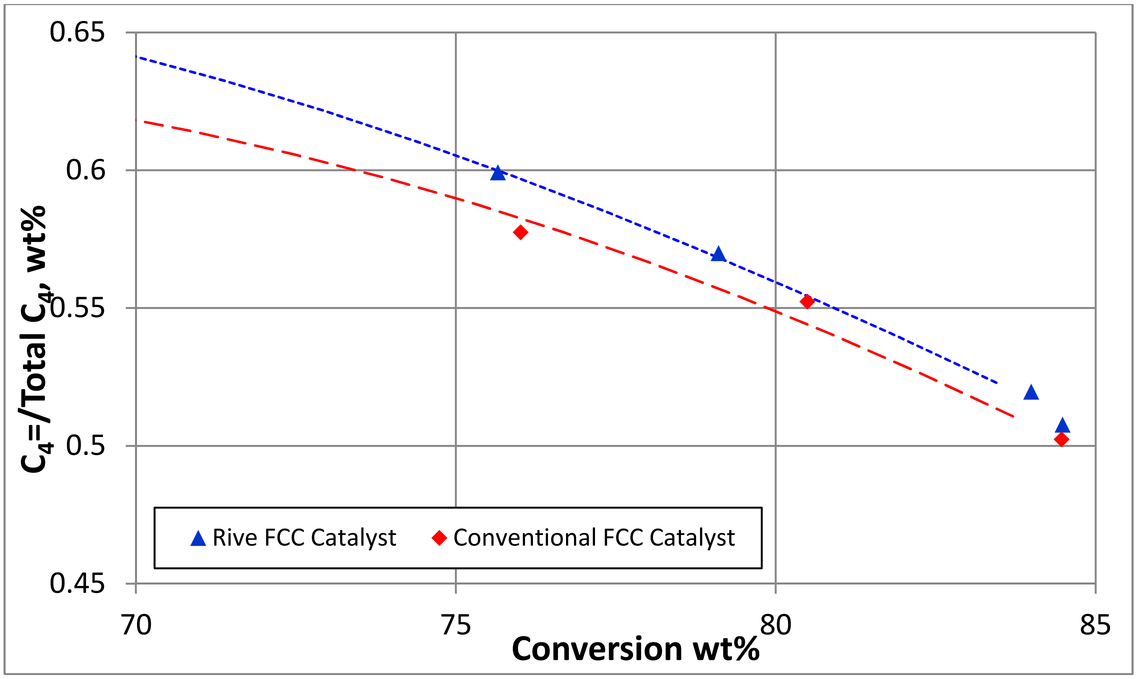

Figure 4: Rive's Effect on C_4 Olefinicity

Rive's FCC catalyst design approach replaces some or all of the catalyst's synthetic pseudoboehmite alumina (active matrix) with mesoporous zeolite. Rive mesopores enable larger feed molecules to enter and crack within the zeolite structure, reducing the need for the matrix alumina. While the matrix surface area (MSA) remains approximately the same as the incumbent for many Rive formulations, (MSA is shifted from the alumina to the zeolite), the zeolite surface area (ZSA) is noticeably higher. Acid sites on zeolites are several orders of magnitude stronger than those on pseudoboehmite alumina; therefore, cracking within the zeolite is more selective and helps to increase the yield of valuable products such as butylenes.

Table 1 shows deactivated ZSA and MSA values for a conventional catalyst formulation and an optimized Rive catalyst formulation. A portion of active matrix was replaced by Rive's mesoporous zeolite, while all other catalyst properties were held constant.

	ZSA (m^2/g)	MSA (m^2/g)	Z/M
Conventional Catalyst	113	73	1.55
Rive Catalyst	169	69	2.45

Table 1: Deactivated Catalyst Zeolite and Matrix Surface Areas

As shown in Figure 5, the optimized Rive catalyst formulation showed a relative boost in C_4 olefinicity of approximately 8% over the conventional catalyst formulation at 75% conversion. A portion of this boost in C_4 olefinicity is due to the Molecular Highways, which allow the butylenes to safely exit the catalyst. There is also a boost in C_4 olefinicity because of the replacement of matrix alumina with Rive zeolite. Total gasoline plus distillate remained approximately the same for both catalyst formulations, and the Rive formulation also provided improved bottoms/coke selectivity and methane/ethane selectivity.

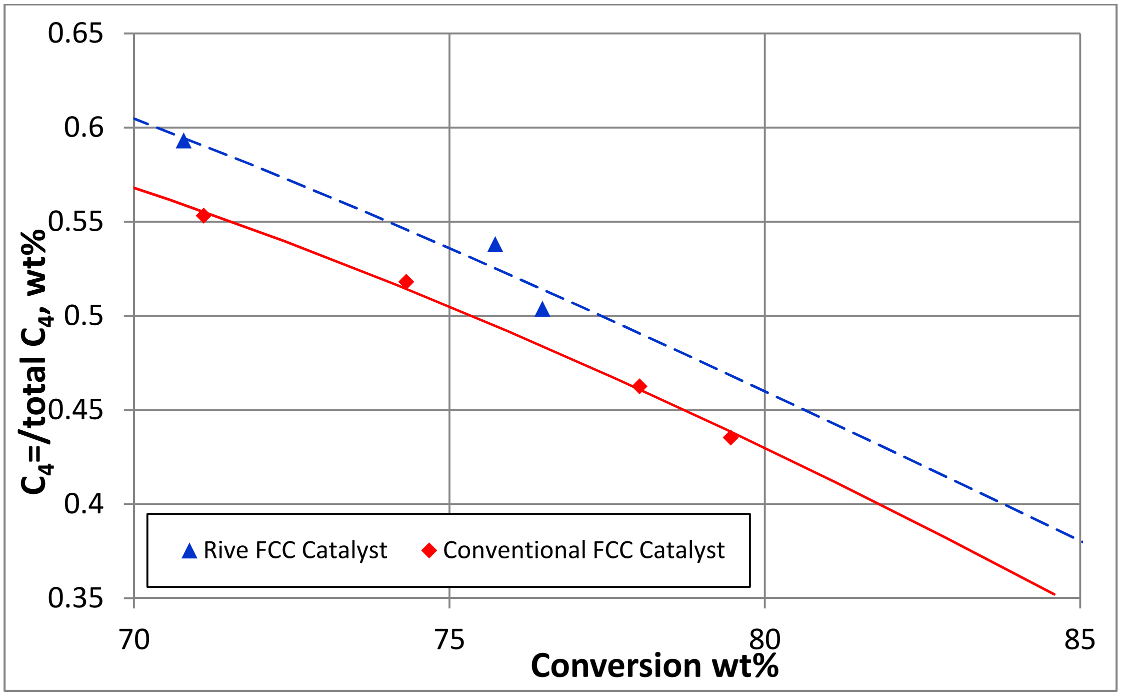

Figure 5: C_4 Olefinicity for Optimized Rive Catalyst Formulation

Commercial Trial

A recent commercial trial conducted in North America had the primary objective of maximizing butylenes for increased alkylation production. Although there was a little room to increase total LPG yield, the goal was to noticeably increase the degree of LPG olefinicity, specifically butylenes.

ACE testing was undertaken at Rive's R&D Center in order to show expectations going into the trial, utilizing commercially produced catalysts which were laboratory deactivated. Results are shown in Table 2.

Catalyst	Incumbent	Rive
C/O	5.79	7.15
Conversion	73.0	73.0
Dry Gas wt%	2.47	2.52
LPG wt%	14.73	15.96
Propane wt%	0.86	0.82
Propylene wt%	4.09	4.53
Butane wt%	4.41	4.34
Butylene wt%	5.38	6.27
Gasoline wt%	51.5	50.8
LCO wt%	20.0	19.6
Bottoms wt%	7.0	7.4
Coke wt%	4.3	3.7
Total	100.0	100.0

Table 2: Rive ACE Results at Constant Conversion

Testing at Grace was carried out in parallel using the same laboratory deactivated catalysts and feed. A comparison of these results (shown in Table 3) reveals excellent consistency in trends such as LPG olefinicity and improved coke selectivity.

Catalyst	Incumbent	Rive
C/O	5.34	6.52
Conversion	69.0	69.0
Dry Gas wt%	1.40	1.50
LPG wt%	13.81	14.77
Propane wt%	0.63	0.61
Propylene wt%	3.90	4.23
Butane wt%	3.92	3.89
Butylene wt%	5.36	6.04
Gasoline wt%	50.6	49.7
LCO wt%	22.5	22.2
Bottoms wt%	8.5	8.8
Coke wt%	3.3	3.1
Total	100.0	100.0

Table 3: Grace ACE Results at Constant Conversion

With the trial underway, close attention was paid to the commercial operation. In support of this, ACE testing of ECAT was carried out on a regular basis as the concentration of Rive catalyst in the circulating inventory steadily increased. Table 4 shows ACE data comparing the incumbent ECAT to that withdrawn at 60% change-over to the Rive catalyst system.

The preferential increase in C_4 olefins compared to C_3 olefins cannot be achieved with a lower unit cell size conventional catalyst. The Rive catalyst also provided a noticeable improvement to CSO/Coke.

	Incumbent ECAT	**Rive ECAT 60% Turnover**
Yields, wt%		
Dry Gas	1.8	1.8
LPG	15.1	15.5
Propane	0.9	0.9
Propylene	4.2	4.4
Butanes	4.8	4.7
Butylenes	5.2	5.5
Gasoline	50.6	50.5
LCO	20.3	20.2
CSO	7.7	7.8
Coke	4.5	4.2
RON	91.2	91.7
MON	80.6	80.8
(R+M)/2	85.9	86.3

Table 4: ACE Results from Commercial ECAT

In line with commercial expectations, ECAT testing indicated an increase in LPG olefinicity (Figure 6), particularly with C_4 olefins (Figure 7). The data provided in these figures spans from the start of the Rive trial until approximately 70% turnover.

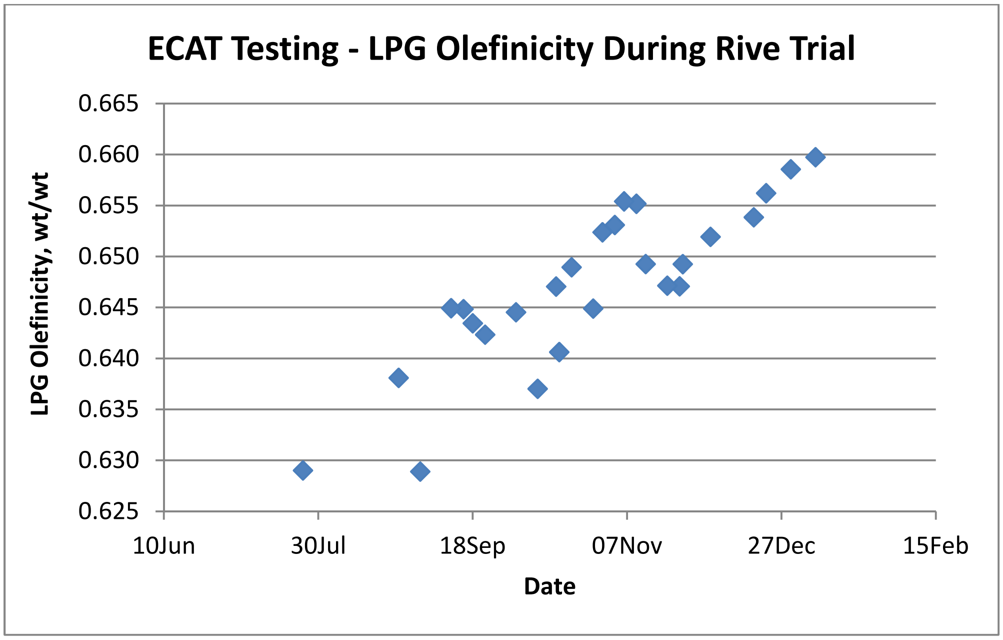

Figure 6: ACE Testing of ECAT Shows Higher LPG Olefinicity with Rive

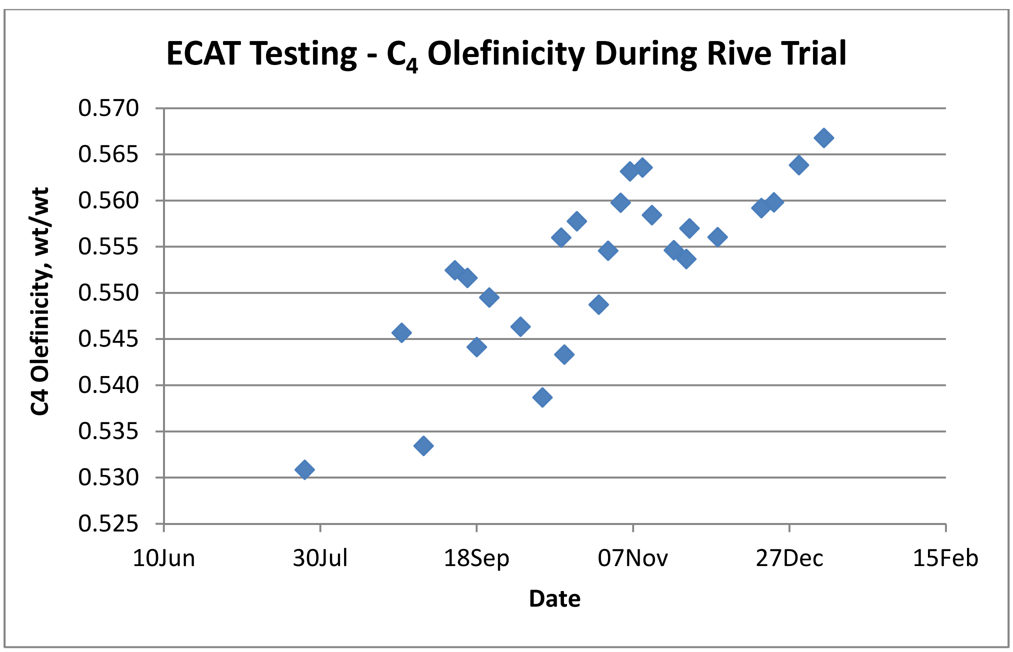

Figure 7: ACE Testing of ECAT Shows Higher C_4 Olefinicity with Rive

Commercial data confirmed the trends observed in ECAT testing. Figure 8 shows the gradual increase in LPG olefinicity as the concentration of Rive catalyst in the circulating inventory steadily increased.

The most important yield shift was the increase in butylenes selectivity as shown in Figure 9.

Gasoline octane also increased due to a higher concentration of olefins in the lighter gasoline fraction (Figure 10).

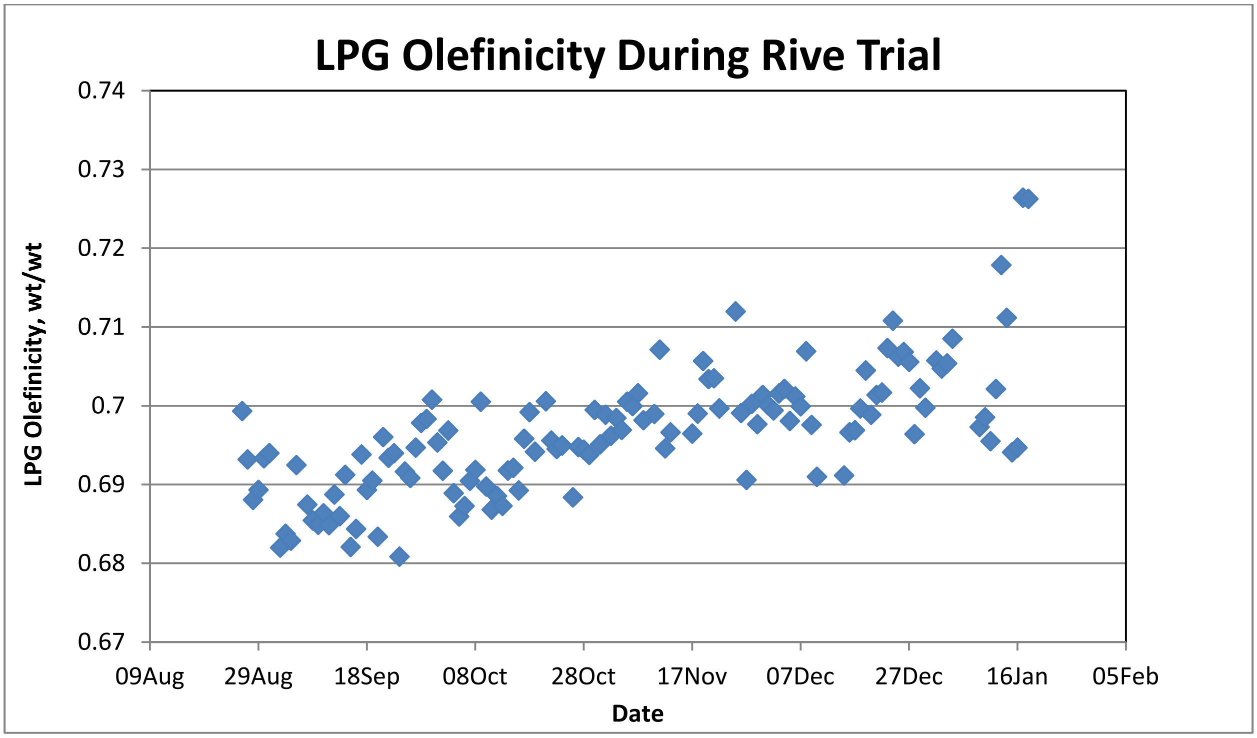

Figure 8: Commercial Yields: LPG Olefinicity

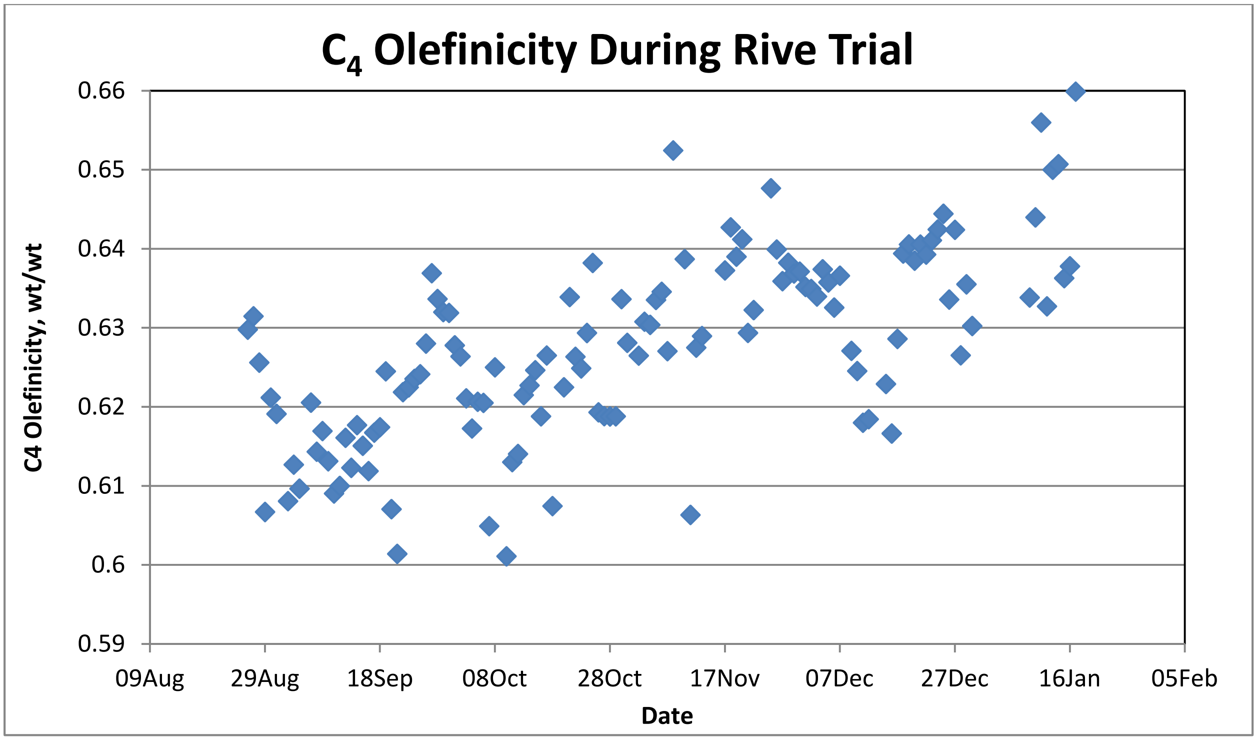

Figure 9: Commercial Yields: C_4 Olefinicity

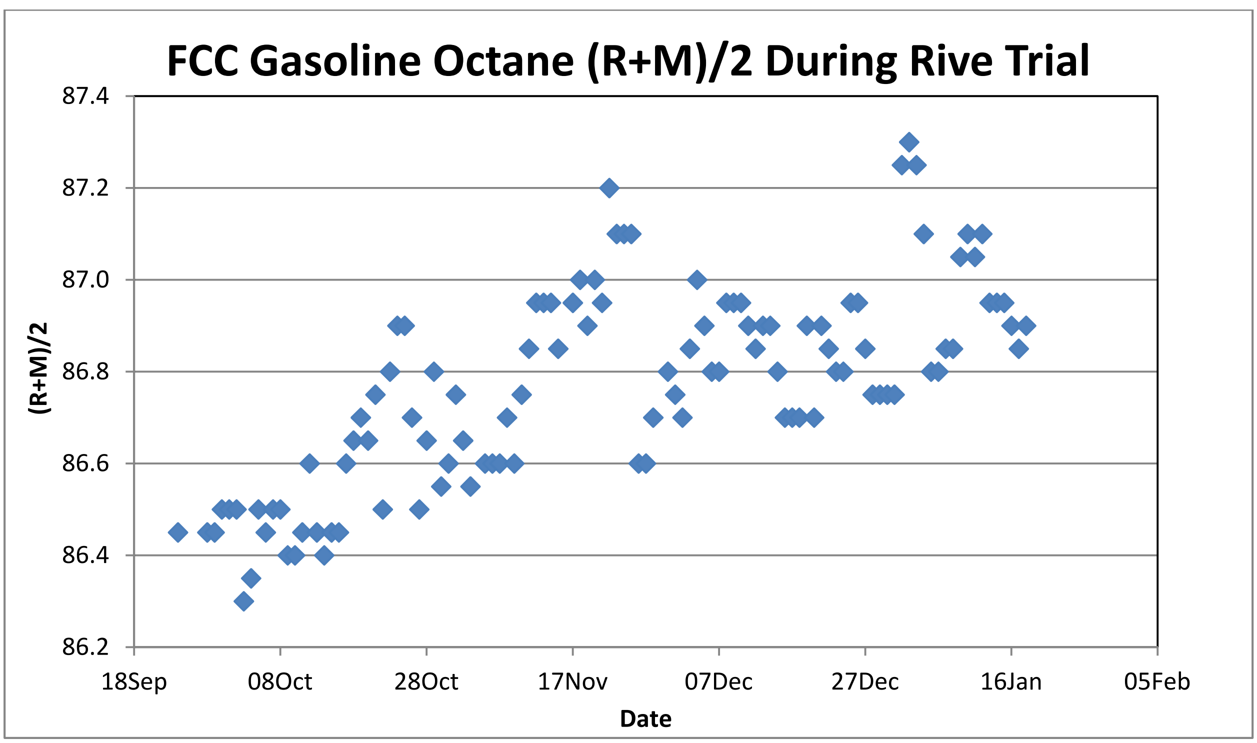

Figure 10: Commercial Yields: FCC Gasoline Octane

Rive/ZSM-5 System Studies

Some refiners in the United States use ZSM-5 additives in their FCC unit to boost gasoline octane and to increase the yield of LPG olefins. ZSM-5 is able to accomplish this by preferentially cracking the low octane olefin components in the C_7–C_{10} range into lighter olefins in the C_2–C_5 range, primarily producing C_3 and C_4 olefins. Additionally, ZSM-5 isomerizes some of the low-octane linear olefins into high-octane branched olefins.

Just as Rive's catalyst quickly channels the highly reactive LPG olefins out of the zeolite, the same occurs for the reactive lower octane gasoline-range olefins. Because FCC gasoline produced from a Rive catalyst is more olefinic in nature than FCC gasoline produced from conventional catalysts, Rive provides more molecules for the ZSM-5 additive to crack and isomerize.

In a continuation of the experiment shown in Figure 3, which quantified the impact of the Rive process on conventional zeolites, 25% of a commercial ZSM-5 additive was added to each of the catalysts and retested. As shown below in Figure 11, the Rive Catalyst with 25% ZSM-5 additive produced the highest degree of C_4 olefinicity. This was particularly noticeable at higher conversion rates.

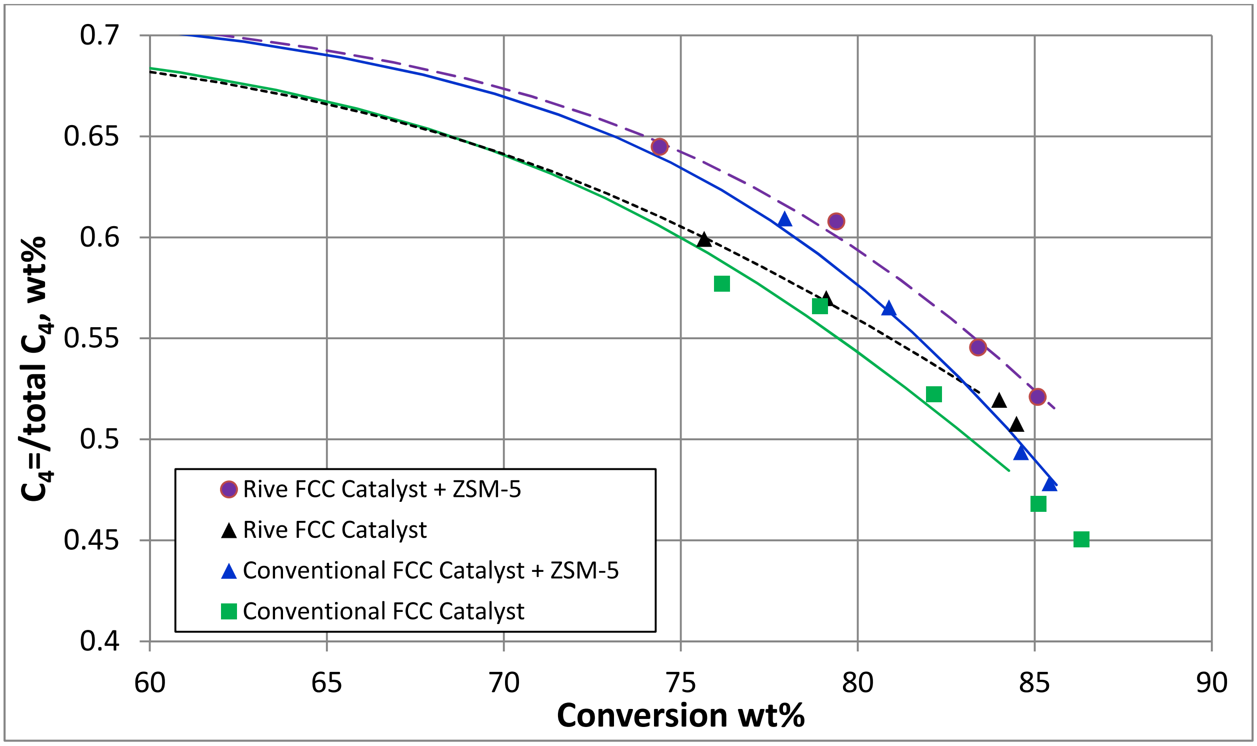

Figure 11: Higher C_4 Olefinicity for Rive Catalysts with ZSM-5 Additive

Rive/ZSM-5 systems were further explored in optimized catalyst formulations, where matrix alumina was replaced with Rive zeolite. As shown below in Figure 12, there was a significant jump in C_4 olefinicity when ZSM-5 was added to the Rive catalyst formulation. At 75% conversion, the C_4 olefinicity using a conventional catalyst increased from 50% to 52% in the presence of ZSM-5, while the C_4 olefinicty using a Rive catalyst increased from 54% to 58% in the presence of ZSM-5.

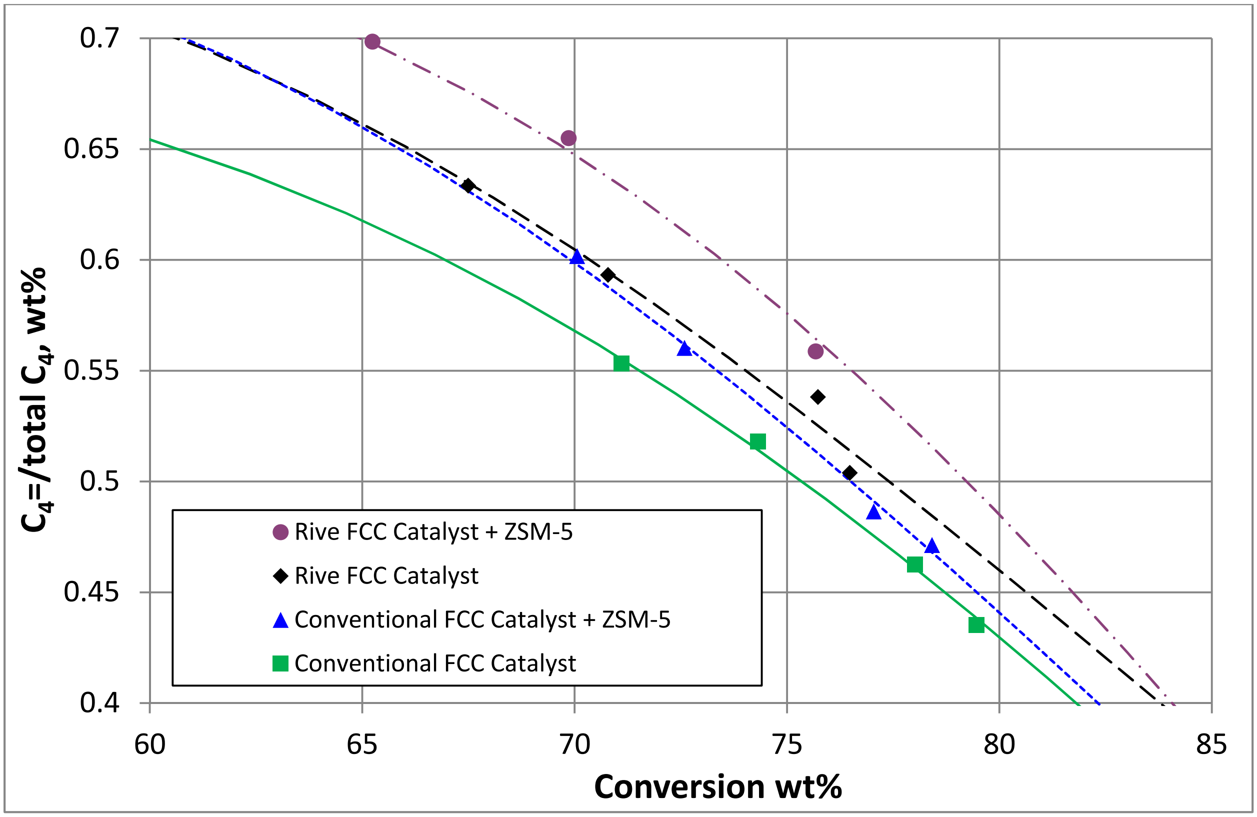

Figure 12: Higher C_4 Olefinicity for Optimized Rive Catalysts with ZSM-5 Additive

For refiners currently utilizing a ZSM-5 additive to increase LPG olefin production or to boost gasoline octane, using a Rive catalyst in conjunction with the ZSM-5 additive will help magnify these gains.

Conclusions:

1. Butylenes are becoming increasingly important to refiners, as it will be imperative to maximize alkylate, a premium blending component in the gasoline pool.

2. Independent laboratory testing has shown that Rive FCC catalysts increase LPG olefinicity - particularly butylenes - without requiring ZSM-5 additives or suffering from reduced total C_3+ liquid volume yields of catalysts with lower unit cell size.

3. ACE testing on deactivated commercial catalyst, commercial ECAT testing, and commercial yields all confirmed that a recent Rive commercial trial provided increased C_4 olefinicity compared to the incumbent catalyst, along with several other significant benefits.

4. Refiners currently using a ZSM-5 additive to increase gasoline octane or production of LPG olefins could realize an additional boost in butylenes yield when the additive is combined with a Rive FCC catalyst system. Rive's FCC gasoline contains more light olefins which can be converted by the ZSM-5 additive into LPG range olefins and high-octane branched olefins.

References:

1. Tier 3 Gasoline Sulfur Standards, United States Office of Transportation and Air Quality, EPA-420-F-14-007, March 2014

2. Evidence of Instracrystalline Mesostructured Porosity in Zeolites by Advanced Gas Sorption, Electron Tomography and Rotational Electron Diffraction, ChemCatChem, 2014

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