“Motiva Unlocks Value in the FCCU through an Innovative Catalyst Solution from Rive and Grace”

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Abstract:

Maximizing diffusion of feed into and products out of an FCC catalyst is critical to unlocking the full value potential of an FCC unit in which the riser residence time is only a few seconds. Through a collaborative effort between Motiva, W.R. Grace & Co. (Grace), and Rive Technology (Rive), an innovative catalyst solution incorporating Rive’s mesoporous zeolite was designed and trialed at a Motiva U.S. Gulf Coast (USGC) refinery\(^1\). This technology engineers a precise series of mesopores into Y zeolite framework, the primary active component of all FCC catalysts, which consequently enhances diffusion of molecules into and out of the catalyst.

The trial results demonstrated the significant value that this technology can bring to an FCC unit. During and since the trial, Motiva has been able to realize uplift in the range of $0.40 to $1.20 /BBL\(_{FF}\) (within the boundary of the FCC unit) depending on the market economics.

This paper will further investigate Rive’s Molecular Highway technology and how it was successfully used to improve performance at a USGC Motiva refinery.

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\(^1\) Rive, Molecular Highway Technology, Grace, ACE, SHARC, and FCC-SIM are all trademarks.
**Catalyst Trial Objectives:**

Based on the potential for high value improvement, Motiva trialed a catalyst designed with Rive’s mesoporous zeolite technology at one of their major USGC refineries. The primary objective of the trial was to increase product revenue while maintaining excellent physical properties of the catalyst. The catalyst’s avenues to improving FCC revenue included:

- Increase total C$_3$+ liquid volume
- Increase LPG olefinicity (both C$_3$ and C$_4$)
- Decrease slurry, dry gas, and coke
- Increase gasoline octane
- Decrease hydrogen in coke

Through a comprehensive ACE testing program and subsequent FCC-SIM modeling and optimization, Grace and Rive developed a catalyst which was designed to meet the refinery’s objectives.

Predicted improvements to the FCC unit during the catalyst trial were as follows:

- Improve coke selectivity, which would boost cat-to-oil by 10% (relative to base)
- Increase C$_3$ and C$_4$ olefinicity by 2% (relative to base)
- Decrease dry gas by 20% (relative to base)
- Similar/ slight increase to gasoline octane
- Similar/ slight decrease to hydrogen in coke
- No increase in catalyst losses despite higher catalyst circulation
- 2.3 vol% increase (absolute) of total C$_3$+ liquid volume
- Value uplift of over $1.00/BBL_ff using base pricing

**Motiva FCC Unit:**

The FCC unit processes a mix of VGO, heavy coker gas oils, and resid. The feed rate is typically pushed to a maximum air blower / supplemental oxygen limit. The catalyst circulation rate could be increased by approximately 10% over base levels before meeting the maximum allowable circulation rate. The FCC base catalyst addition is 50% fresh catalyst and 50% purchased Ecat. Purchased Ecat is used to assist with metals management.
Rive’s Molecular Highway™ Technology:

Rive and Grace jointly developed and commercialized Molecular Highway™ technology for use in FCC units throughout North America and Europe. The “Rive” process introduces a vast network of intermediate-sized (~40 angstroms) mesopores into the zeolite, which significantly enhances diffusion of the feed and cracked products in the catalyst.

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

![Figure 1: Photomicrographs of Conventional Zeolite (left) and Rive Zeolite (right)](image)

Importantly, the mesopores shown above in the Rive zeolites are homogeneously distributed and interconnected within the zeolite. Stockholm University recently used more novel imaging techniques to investigate the internal architecture of Rive’s zeolite. ¹

Electron tomography and rotational electron diffraction were utilized to provide an unprecedented look inside the zeolite crystal, as shown in Figure 2. These 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. ¹
Electron tomography and rotational electron diffraction by Stockholm University show Rive’s network of mesopores are interconnected and extend throughout the zeolite.

As a result of Rive’s interconnected network of mesopores, larger feed molecules which vaporize in the FCC unit at temperatures above 950°F are able to access the zeolite. The 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 over-cracking into dry gas, olefin saturation via hydrogen transfer, or coke formation via condensation reactions. These concepts are illustrated below in Figure 3.

**Figure 2: Molecular Highways in Rive Zeolite**

**Figure 3: Overview of Rive’s Molecular Highway™ Technology**

The mesopores engineered into Rive’s zeolite allow access and more selective catalytic cracking to larger feed molecules, while allowing the valuable cracked products to quickly exit the zeolite.
FCC catalyst formulations containing Rive zeolite typically show several benefits compared to catalysts containing conventional zeolites. These benefits 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 air blower rate, wet gas compressor rate, and regenerator temperature.

Two previously documented Rive commercial operations have been captured in American Fuel & Petrochemical Manufacturers (AFPM) papers AM-13-03 and AM-12-25.²,³

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 molecules must travel across longer diffusion path lengths, they can become saturated through hydrogen transfer reactions into less-valuable LPG paraffins, over-crack into dry gas, or condense within the catalyst pores to form coke. Rive’s intermediate-size mesopores have been proven to allow rapid transport of these valuable LPG olefins out of the zeolite, thereby enhancing LPG olefinicity.

The Rive catalyst for this operation included 1% ZSM-5. The purchased Ecat (50% of total Ecatal) contained a significant amount of ZSM-5.
Rive/Grace Catalyst Trial Data:

In the following sections, the feed rate/ quality, operating conditions, and Ecat data observed during the Rive/Grace catalyst trial will be discussed.

FCC Feed Data:

The total FCC feed rate, relative to normal operation (base) throughput, is shown in Figure 4. Feed rate was decreased at times due to irregular refinery operation, such as during maintenance of other process units. Feed rate was pushed beyond base throughput when dictated by refinery economics. FCC operation was very stable at feed rates 10-15 KBPD above the base feed rate.

![Figure 4: Total FCC Feed Rate](image)

This figure illustrates the variations to FCC feed throughput during the catalyst trial. Feed rate typically varied between +/- 10 KBPD of normal (base) operation. FCC operation with Rive/Grace was stable at the very high feed rates observed during October and November.

As shown in Figures 5A-D, fresh feed quality varied during the trial, particularly during periods of irregular operation. API and CCR generally remained in similar ranges as before the trial; however, basic nitrogen in the feed increased by approximately 50 ppm during the trial, which would typically lead to a loss of approximately 0.5 wt% conversion. The feed K factor, a measure of feed crackability, was generally lower during the trial, which indicated a more naphthenic feed, which is more difficult to crack.
Figure 5A: Fresh Feed API

This figure depicts the changes in fresh feed API throughput the trial. The feed API averaged similar values for the incumbent and Rive/Grace catalysts.

Figure 5B: Fresh Feed CCR

This figure depicts the changes in fresh feed CCR throughput the trial. The feed CCR averaged similar values for the incumbent and Rive/Grace catalysts.
Figure 5C: Fresh Feed Basic Nitrogen
This figure depicts the changes in fresh feed basic nitrogen throughout the trial. Basic nitrogen during the trial was approximately 50 ppm higher than the base feed quality.

Figure 5D: Fresh Feed K Factor
This figure depicts the changes in fresh feed K factor throughout the trial. The lower K factor during most of the trial was indicative of less crackable feed (more naphthenic, less paraffinic than base feed quality).
FCC Operating Data:

Rive, Grace, and Motiva closely monitored daily operating data throughout the trial to evaluate the effects of the catalyst change.

Improvement to coke selectivity was observed early in the trial, as the catalyst circulation rate and cat-to-oil ratio (C/O) increased while the regenerator temperature decreased. Since the C/O varied strongly with feed rate fluctuations, a cross-plot of C/O vs. total feed rate is provided in Figure 6. At the base feed rate, the Rive/Grace C/O was 12% higher than the incumbent catalyst.

Figure 6: C/O vs. Total Feed Rate (KBPD)

A cross-plot of cat-to-oil (C/O) vs. total feed rate indicates the Rive/Grace catalyst provided 12% higher C/O for the base feed rate. This is a result of the improved coke selectivity of the Rive/Grace catalyst.

Another effect of improved coke selectivity is decreased regenerator temperature. At the base riser temperature, the regenerator bed temperature was 20°F lower than with the incumbent catalyst (Figure 7). Lower regenerator temperature is beneficial for reducing dry gas, reducing deactivation of Ecat, reducing SOx emissions, and improving overall mechanical reliability in the regenerator.
Figure 7: Regenerator Dense Bed Temperature
This figure shows a cross-plot of regenerator bed temperature vs. riser outlet temperature. At the base riser outlet temperature, the regenerator temperature was 20°F lower for the Rive/Grace catalyst.

As shown in Figure 8, dry gas yield decreased by 6% relative to the incumbent catalyst at the base riser outlet temperature. The Rive zeolite allowed the valuable, reactive LPG olefins to more easily exit the zeolite instead of over-cracking into dry gas.

Figure 8: Dry Gas Yield
This figure shows a cross-plot of dry gas yield vs. riser outlet temperature. At the base riser outlet temperature, the dry gas was 6% lower (relative) for the Rive/Grace catalyst.
As a result of the higher C/O and reduced dry gas production, C₃+ total liquid volume increased during the trial, as shown in Figure 9. The following cross-plot helps to compare improvements to C₃+ total liquid volume for a given feed rate. At the base feed throughput, the C₃+ total liquid volume increased by 1.5 vol% on average.

![Figure 9: C₃+ Total Liquid Volume vs. Total Feed Rate](image)

This figure shows the total C₃+ liquid volume % produced, as a function of total feed rate. For the base feed rate, the Rive/Grace catalyst produced 1.5 vol% more valuable liquid product on average than the incumbent catalyst.

As shown in Figures 10 and 11, both C₃ and C₄ olefinicities increased during the trial, which added substantial value to the refinery’s LPG products. At a base riser temperature, C₃ and C₄ olefinicities increased by approximately 2% and 4% (relative to base), respectively.

The P₂O₅ contents measured on Ecats were similar (on average) for both the incumbent and Rive/Grace catalysts, so LPG olefinicity increases were not a result of changes in stabilized ZSM-5 additive usage. Additionally, the boost to butylenes was greater than the boost to propylene, which is an opposite trend than what is typically observed from increased ZSM-5 additive usage.

C₃ olefinicity was not affected by riser temperature as much as C₄ olefinicity due to the significant presence of ZSM-5 in the purchased Ecats.
Figure 10: C$_3$ Olefinicity vs. Riser Outlet Temperature
C$_3$ olefinicity increased by approximately 2% (relative) with the Rive/Grace catalyst.

Figure 11: C$_4$ Olefinicity vs. Riser Outlet Temperature
C$_4$ olefinicity increased by approximately 4% (relative) with the Rive/Grace catalyst.
Even with changes in operation that should have directionally increased hydrogen in coke (reduction in ratio of stripping steam usage to catalyst circulation), the hydrogen in coke decreased during the trial, as shown in Figure 12. For a constant ratio of stripping steam to catalyst circulation, the hydrogen in coke decreased by 15% (relative to base). This is a testament to the improved diffusional properties and strippability of the Rive/Grace catalyst.

Benefits to improved stripping include additional recovery of valuable hydrocarbons, lower regenerator temperature, higher cat-to-oil, and lower partial pressure of steam in regenerator (improved zeolite stability).

Despite reduced stripping steam and higher circulation, the hydrogen in coke decreased by 15% (relative) with the Rive/Grace catalyst. This can be attributed to the catalyst's improved diffusional properties.

Another effect of the catalyst’s improved coke selectivity was reduction of carbon on regenerated catalyst (CRC) throughout the trial. Since the carbon deposited on the spent catalyst decreased, the Ecat was burned cleaner in the regenerator, which yielded a lower CRC. The CRC was reduced from approximately 0.25 wt% to 0.10 wt% during the trial, which increased the amount of available acid sites on the regenerated catalyst.
Figure 13: Carbon on regenerated catalyst (CRC)
The CRC decreased during the trial as another response to the catalyst's improved coke selectivity. This provided cleaner regenerated catalyst to contact the fresh feed in the riser.

Although the catalyst circulation rate increased by more than 10% during the trial, ash in slurry (an indicator of catalyst attrition/loss) did not increase.

Figure 14: Slurry Ash
Slurry ash was unchanged during the Rive/Grace trial.
**Ecat Data:**

Ecat analysis was useful in separating the effects of the catalyst change from the continuously changing feed quality and operating conditions at the refinery. Ecat analysis involved testing at fixed ACE conditions and a fixed reference feedstock. Coke factor, Gas factor, and Fluidization factor are discussed in this section.

**Coke Factor:**

The coke factor is a measure of the Ecat’s coke selectivity compared to a steam-deactivated reference catalyst at the same conversion. Lower coke factors translate commercially into lower delta coke, lower regenerator temperature, and higher cat-to-oil. The coke factor decreased from an average of 1.2 with the incumbent catalyst to 1.1 with the Rive/Grace catalyst. As demonstrated commercially, the delta coke and regenerator temperature decreased during the trial, while the cat-to-oil increased.

![Coke Factor Chart](image)

**Figure 15: Ecat Coke Factor**

The Ecat coke factor was approximately 8% lower for the Rive/Grace catalyst. This is indicative of the Rive/Grace catalyst’s improved coke selectivity, which manifested in the unit operation.
**Gas Factor:**

The gas factor is a measure of the Ecat’s tendency to produce hydrogen compared to methane. It is greatly affected by the metals level on the Ecat, particularly in regard to the concentration of nickel. During the trial, the ratio of antimony-to-nickel decreased from an average of 0.20 to 0.17. Still, the gas factor fell considerably with the Rive/Grace catalyst for a given ratio of Sb/Ni. Using 20% less antimony (Sb/Ni ratio of 0.17), the Rive/Grace Ecat achieved a similar gas factor (3.2) to the incumbent Ecat (Sb/Ni ratio of 0.21).

![Gas Factor vs. Sb/Ni](image)

**Figure 16: Ecat Gas Factor**

The Rive/Grace Ecat achieved a normal gas factor (3.2) with a Sb/Ni ratio of just 0.17 instead of 0.21. This represents the reduced dehydrogenation and gas-making tendencies of the Rive/Grace catalyst, which were commercially confirmed in the unit from lower dry gas and hydrogen production.
**Fluidization Factor:**

The fluidization factor is a measure of the fluidization characteristics of the Ecat\(^4\). An Ecat having a higher fluidization factor can typically provide more reliable catalyst circulation commercially, leading to improved operability in standpipes and slide valves. This can also provide improved diffusion/heat transfer between the catalyst and feed. The fluidization factor increased from an average of 3.08 with the incumbent catalyst to 3.20 with the Rive/Grace catalyst.

![Fluidization Factor](image)

**Figure 17: Ecat Fluidization Factor**

The Ecat fluidization factor increased with the Rive/Grace catalyst, which typically leads to more reliable catalyst circulation and improved heat transfer between the catalyst and feed.
**Benchmark ACE Testing:**

Rive/Grace performed an ACE study on Ecat samples using Motiva feed collected just prior to the trial. The study evaluated the following Ecats:

- Pre-trial incumbent Ecat
- 35% turn-over (T/O) Rive/Grace Ecat (Rive/Grace catalyst cannot surpass 50% unit T/O since fresh and purchased catalyst addition rates are equal)

Ecat properties are provided in Table 1. Green arrows for the 35% T/O Ecat sample represent advantaged metals compared to the pre-trial Ecat, while red arrows indicate disadvantaged metals compared to the pre-trial Ecat.

<table>
<thead>
<tr>
<th></th>
<th>Ni, ppm</th>
<th>V, ppm</th>
<th>Sb, ppm</th>
<th>Sb/Ni</th>
<th>P2O5, ppm</th>
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<tbody>
<tr>
<td><strong>Pre-trial E-cat</strong></td>
<td>2863</td>
<td>4189</td>
<td>615</td>
<td>0.21</td>
<td>8600</td>
</tr>
<tr>
<td><strong>35% Rive T/O E-cat</strong></td>
<td>3096↑</td>
<td>3665↓</td>
<td>547</td>
<td>0.18↓</td>
<td>7100↓</td>
</tr>
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</table>

**Table 1: Ecat properties from Benchmark ACE Test**

This table provides properties for the Ecat samples from the benchmark ACE study, comparing pre-trial Ecat with 35% Rive/Grace Ecat (70% replacement of incumbent fresh catalyst)

Table 2 provides ACE results of the Ecat samples run at constant conversion of 70%. Highlights between the incumbent Ecat and the 35% T/O Grace/Rive Ecat are as follows:

- Total LPG yield increased from 17.1 wt% to 17.9 wt%.
- All LPG paraffin yields were lower, while all LPG olefin yields were higher. C3 olefinicity increased by 3% (relative to base), while C4 olefinicity increased by 4% (relative to base). The increased LPG olefinicities occurred with less P2O5 on Ecat, as noted in Table 1.
- Total Gasoline + LCO yield decreased by 0.5 wt%, which was converted predominantly into valuable LPG olefins.
- Coke yield decreased from 6.9 wt% to 6.5 wt%. Commercially, this translated into lower delta coke, lower regenerator temperature, and increased circulation.
- Gasoline octane increased slightly from 87.85 to 88.00 (R+M)/2.
- While dry gas yield increased slightly from 2.2 wt% to 2.3 wt%, Sb/Ni on Ecat was 15% lower for the Rive/Grace Ecat, as noted in Table 1. Commercially, the lower regenerator temperature further assisted in reducing dry gas.
Table 2: Benchmark ACE Test Results

This table provides ACE yields from the benchmark ACE study, comparing pre-trial Ecats with 35% Rive/Grace Ecats (70% replacement of incumbent fresh catalyst). Green arrows indicate desirable shifts while red arrows indicate undesirable shifts. These results confirm improvements observed in the plant.

<table>
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<tr>
<th></th>
<th>Pre-trial Ecat</th>
<th>35% T/O Ecat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>C/O</td>
<td>5.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Total Dry Gas, wt%</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Propane, wt%</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Propylene, wt%</td>
<td>5.4</td>
<td>6.1</td>
</tr>
<tr>
<td>Iso-Butane, wt%</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td>N-Butane, wt%</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Butylene, wt%</td>
<td>6.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Total LPG, wt%</td>
<td>17.1</td>
<td>17.9</td>
</tr>
<tr>
<td>Gasoline, wt%</td>
<td>43.9</td>
<td>43.3</td>
</tr>
<tr>
<td>LCO, wt%</td>
<td>20.6</td>
<td>20.7</td>
</tr>
<tr>
<td>Bottoms, wt%</td>
<td>9.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>6.9</td>
<td>6.5</td>
</tr>
<tr>
<td>C₃Olefinicity, wt%/wt%</td>
<td>84.4</td>
<td>87.1</td>
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<td>C₄Olefinicity, wt%/wt%</td>
<td>60.7</td>
<td>63.3</td>
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<tr>
<td>Total LPG Olefinicity, wt%/wt%</td>
<td>69.6</td>
<td>72.6</td>
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<tr>
<td>Total Gasoline Octane, (R+M)/2</td>
<td>87.85</td>
<td>88.00</td>
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</table>
Rive/Grace Trial Uplift:

Uplift during the Rive/Grace catalyst trial was evaluated using several methods. These methods include:

- Shell proprietary SHARC simulation
- Rive/Grace FCC-SIM simulation
- Rive/Grace benchmark ACE testing
- Motiva look-back tool

The SHARC and FCC-SIM models were in agreement that the Rive/Grace catalyst provided significant value improvement for Motiva. Contributors to value improvement included (a) increased C₃+ total liquid volume, (b) increased LPG olefinicity (particularly C₄), (c) decreased dry gas, and (d) decreased hydrogen in coke. The Motiva refinery was able to realize uplift in the range of $0.40 to $1.20 /BBL_{FF} (within the boundary of the FCC unit), depending on the market economics. The value uplift was slightly less than projected at the start of the trial due to unrealized limitations of total LPG production.

Uplift was further validated from modeling the results of the benchmark Ecat ACE results in Table 2, which compared the pre-trial Ecat against the Rive/Grace Ecat.

Motiva created a unique look-back tool, which could evaluate FCC profitability for periods of similar operation between the incumbent catalyst and Grace/Rive catalyst. Profitability was evaluated for periods of time when the feed rate, fresh and purchased catalyst addition rates, feed quality, operating conditions, and LPG production were all similar. This evaluation tool was helpful to isolate and confirm the value realized by the refinery as a result of the catalyst change.

Technical Service:

Collaboration between the Motiva refinery, Rive, and Grace was excellent throughout the catalyst trial. The objective of the entire team was to push the unit to maximum profitability, by leveraging the catalyst’s benefits at optimized operating conditions.

Weekly teleconferences, monthly data reviews at the refinery, active Action Item Logs, and a true dedication by all to refinery improvement were keys to the trial’s success.
Looking Forward:

After the trial’s completion in late 2016, a continued supply agreement was reached between Rive/Grace and Motiva. Based on mutual learnings from our combined team, as well as predicted changes to feed quality, product pricing, and unit constraints such as total LPG production, an optimized Rive/Grace catalyst formulation was developed for the refinery. The close relationship between all parties and the new custom catalyst formulation are expected to continue to drive unit improvement and product revenue for Motiva.

Conclusions:

1. The results from this commercial FCC catalyst trial support Rive’s assertion that increasing diffusion of feed into and products out of an FCC catalyst is critical to unlocking the full value potential of an FCC unit, in which the riser residence time is only a few seconds.

2. Grace/Rive designed a catalyst for a trial at a major USGC Motiva refinery in 2016. In line with the refinery’s objectives, the following FCC performance improvements were documented at normal operating conditions, relative to pre-trial conditions.

   a. Cat-to-oil increased by 12%
   b. Total C₃+ liquid volume increased by 1.5 vol%
   c. Regenerator temperature decreased by 20°F for a base riser temperature
   d. Dry gas decreased by 6% for a base riser temperature
   e. C₃ olefinicity increased by 2% for a base riser temperature
   f. C₄ olefinicity increased by 4% for a base riser temperature
   g. Hydrogen in coke decreased by 15%
   h. Carbon on regenerated catalyst (CRC) decreased by 60%

3. Extensive FCC modeling with both FCC-SIM and SHARC, Ecat benchmark ACE testing, and operating data comparison between periods of similar operation confirmed that Motiva realized uplift in the range of $0.40 to $1.20 /BBL₉₉ (within the boundary of the FCC unit), depending on feed quality and market economics.

4. As a result of the demonstrated performance improvements and strong technical service relationship between Motiva, Grace, and Rive, a continued supply agreement with an optimized catalyst formulation was executed following the trial.
References:


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The authors wish to acknowledge with sincere appreciation and thank the entire team from Grace for their collaboration, expertise, and support of the research and development described in this paper.

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