



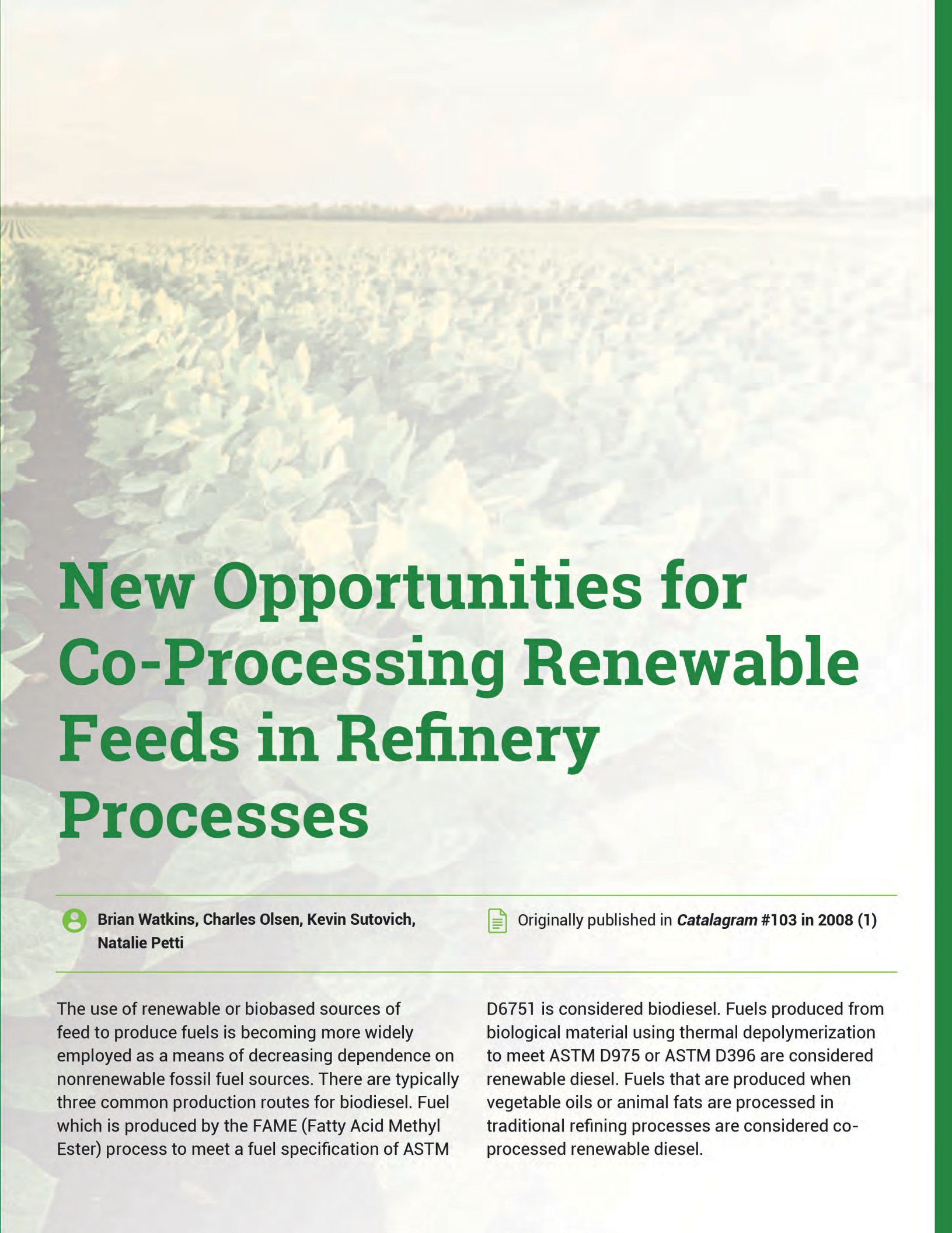
**Rapid decarbonization of the way we live requires the use of existing assets and processes.** Co-processing of biomass-derived feedstocks in refining processes reduces the carbon intensity of transportation fuels and gained significant momentum in the 2020's. Co-processing is forecasted to increase with the progression of government mandates and incentives and as renewable feedstock becomes more available. Co-processing of bioderived feedstocks is being trialed and implemented around the world with some regional differences.

The article here, published in the Spring 2008 *Catalagram*, discusses biofeed composition, contaminants, and reaction chemistry in hydroprocessing and FCC units. Though the focus was on first generation biofeeds (edible oils) at the time of publication, the discussed effects are valid for the co-processing of second generation biofeedstocks like waste cooking oils, animal fats and other fats, oils and greases (FOGs).

ART Hydroprocessing and Grace FCC catalyst technologies are used in numerous co-processing applications around the world and have proven to support optimum refinery profitability by meeting activity, stability and selectivity requirements in biofeed co-processing. This iconic paper has been the basis for the multiple successful applications in the last 15 years and guides the industry on its endeavor to explore new unconventional feedstock applications.



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# New Opportunities for Co-Processing Renewable Feeds in Refinery Processes

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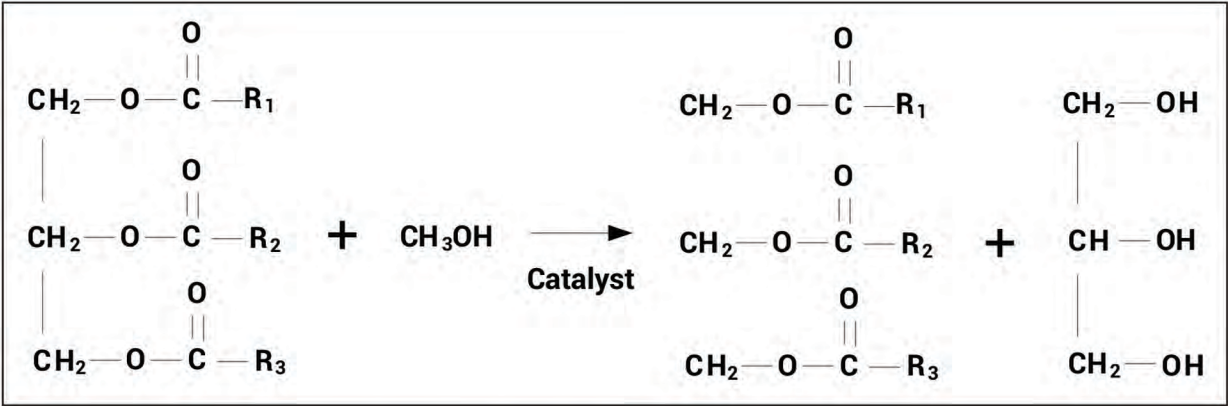
 Originally published in **Catalagram #103 in 2008 (1)**

The use of renewable or biobased sources of feed to produce fuels is becoming more widely employed as a means of decreasing dependence on nonrenewable fossil fuel sources. There are typically three common production routes for biodiesel. Fuel which is produced by the FAME (Fatty Acid Methyl Ester) process to meet a fuel specification of ASTM

D6751 is considered biodiesel. Fuels produced from biological material using thermal depolymerization to meet ASTM D975 or ASTM D396 are considered renewable diesel. Fuels that are produced when vegetable oils or animal fats are processed in traditional refining processes are considered co-processed renewable diesel.



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|                           | Soybean Oil | Rapeseed Oil | *Palm Oil |
|---------------------------|-------------|--------------|-----------|
| API (°)                   | 21.58       | 21.98        | 22.98     |
| Specific Gravity (g/cc)   | 21.6        | 22.0         | 23.0      |
| Sulfur, ppm               | 0           | 3            | 1         |
| Oxygen, wt%               | 10.5        | 10.62        | 11.33     |
| Nitrogen, ppm             | 3.9         | 16           | 1.6       |
| D2887 Distillation, °F    |             |              |           |
| IBP                       | 702         | 710          | 625       |
| 5%                        | 1059        | 1065         | 941       |
| 10%                       | 1069        | 1077         | 1026      |
| 30%                       | 1090        | 1095         | 1062      |
| 50%                       | 1102        | 1106         | 1079      |
| 70%                       | 1111        | 1115         | 1090      |
| 90%                       | 1183        | 1188         | 1146      |
| 95%                       | 1232        | 1238         | 1197      |
| FBR                       | 1301        | 1311         | 1302      |
| Metals Contamination, ppm |             |              |           |
| Na                        | 2.0         | 4.7          | 0.0       |
| Ca                        | 3.0         | 13.8         | 0.0       |
| Mg                        | 0.9         | 0.3          | 0.0       |
| P                         | 6.5         | 4.0          | 0.0       |
| Zn                        | 0.1         | 0.6          | 0.0       |
| Al                        | 0.1         | 0.2          | 0.0       |
| Mn                        | 0.0         | 0.1          | 0.0       |

\* Oil was pre-processed to remove impurities

Table 2. Analysis of Different Biofeed Sources

At these levels ART's high capacity guard materials and Grace Davison specialty catalysts are capable of protecting the downstream high activity catalysts from these damaging poisons.

Since these renewable feeds are derived from a biological source, they also contain a high concentration of oxygen. For the materials listed in Table 1 the oxygen content ranges from 10 to 15%, and is entirely dependent on the length and degree of saturation of the fatty acid chains.

This quantity of oxygen is important, as under normal hydrotreating conditions the oxygen will react with the hydrogen to form water. This water, if generated in a significant enough quantity, may cause problems such as weakening the catalyst support or redistribution of the active metals and

loss of surface area. At the expected blending ratios of 10%, the oxygen content is around 1 to 1.5 wt%, and even if all the oxygen is converted, this is unlikely to generate enough water to be a significant problem.

### General Co-Processing Ideas

Looking at these compounds from a hydrotreating perspective, the biofeeds can be classified as mono and di-olefins, since a majority of these compounds have one or two double bonds per fatty acid chain with a few having three. Using the numbers listed in Table 1, palm oil has an average of 1.1 double bonds per chain, rapeseed oil has 1.3 and soybean oil has 1.7. It has been widely established that the olefin saturation reactions occur quite rapidly and tend to happen near the top of the catalyst bed in a hydrotreater. The reactions go to near completion at typical hydrotreating conditions, and will generate between 130-150 BTU's per standard cubic foot of hydrogen consumed. The reaction pathways to hydrotreat the bio-oils is shown in Figure 3. In the first step of the reaction, the unsaturated fatty acid chains are quickly converted into fully saturated n-paraffins. The second reaction that must occur in order to ensure that the compounds will be of the appropriate size for the diesel pool is the breaking of the fatty acid chains away from the glycerin molecule which requires cleavage of a carbon – oxygen bond.

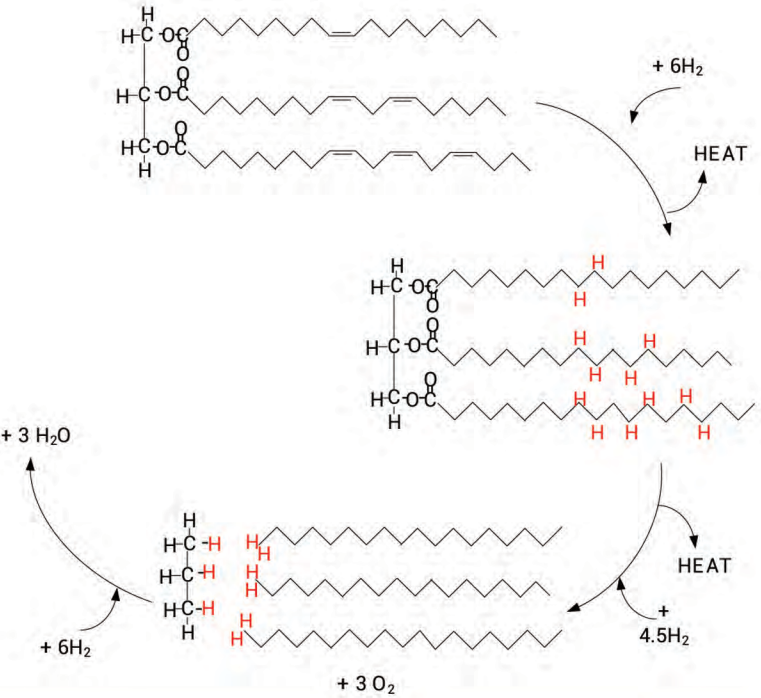


Figure 3. Pathways to Hydrotreating of Renewable Oils

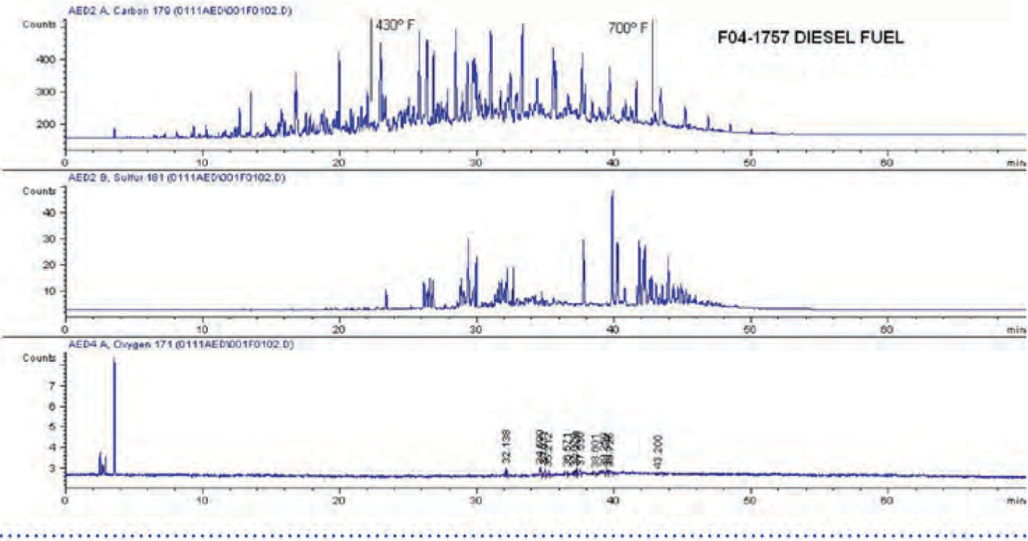


Figure 4. Chromatogram of Sulfur, Carbon & Oxygen in a Diesel Feedstock

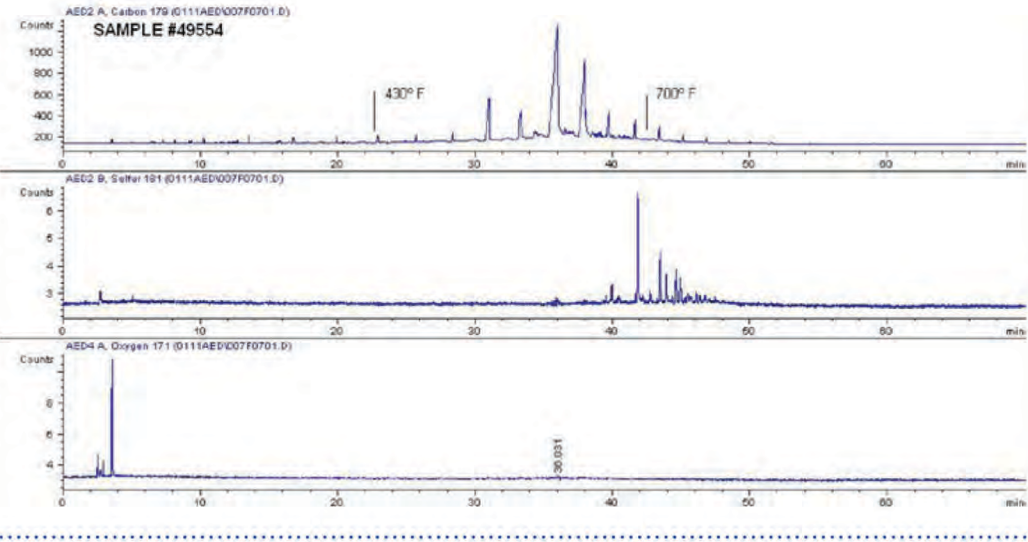


Figure 5. Chromatogram of Sulfur, Carbon and Oxygen in a Co-Processed Product

This reaction is expected to take place at a rate similar to that of sulfur compounds such as sulfides and disulfides. In order to verify that this is indeed the reaction that is taking place, several different feed sources were analyzed for oxygen in order better understand where they are likely to be distributed in the feeds. This analysis has a detection limit of approximately 2.6 ppm oxygen. Figure 4 is a Carbon-Sulfur-Oxygen chromatogram for a diesel feedstock that contains 263 ppm oxygen.

Analytical techniques using GCAED have shown that in normal ULSD operation, no oxygen is detected in the products

at levels below 500 ppm sulfur. This can be seen in Figure 5 which shows the analysis of one of the co-processed products which has a total sulfur of 31 ppm and less than 1 ppm nitrogen.

### Pilot Plant Testing of Renewable Oils

In order to understand the process for co-treating renewable fuel components in a hydrotreater, ART completed a number of pilot plant studies. A wide range of ULSD operating conditions were investigated to determine if there is an optimal operating window for

processing these types of feeds. The conditions included hydrogen pressures from 450 to 1100 psia and hydrogen to oil ratios of 1000 to 3000 SCFB.

The three different renewable sources of oil were blended in separately with a typical straight run (SR) diesel feedstock. The renewable component level was varied from 10% to 80% and hydrotreated over the range of processing conditions listed here. The SR component properties are listed in Table 3, along with 5 different blends of the bio components. As can be seen in the table, the effects of blending in the renewable source are to dilute the sulfur, nitrogen and aromatic contents and decrease the API gravity.

ART then conducted testing on blends containing the various renewable sources of feedstock at the targeted 10% level. Figure 6 summarizes some of the results of the testing. The testing showed that soybean and rapeseed oils behave similarly when co-processed in a SR diesel. The feed blends required essentially the same temperature for 10 ppm product sulfur, and the apparent activation energy (temperature response) for the two feed blends is similar to that of the SR feedstock alone. The palm based oil, which had been previously processed, was apparently easier to treat to low sulfur diesel levels, but for 10 ppm product sulfur the temperature was only slightly lower than that for the SR feed. The apparent activation energy for this feed blend was lower than the SR component indicating the temperature response in the unit was lower. Comparing the feeds at ultra low sulfur levels suggests the co-processing of the renewable oils has only a small effect on the performance of the hydrotreater. The data indicates that the least reactive blend contains rapeseed oil, followed by the soybean oil blend and finally the palm oil blend. The difference, however, is only about 10°F for <10 ppm product sulfur.



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|                        | SR Oil | 10% Soybean | 10% Palm | 10% Rapeseed | 40% Soybean | 80% Soybean |
|------------------------|--------|-------------|----------|--------------|-------------|-------------|
| API                    | 34.44  | 33.03       | 33.50    | 33.29        | 29.24       | 24.38       |
| Specific Gravity, g/cc | 0.852  | 0.859       | 0.857    | 0.858        | 0.879       | 0.907       |
| Sulfur, wt%            | 1.123  | 1.083       | 1.092    | 1.042        | 0.670       | 0.210       |
| Nitrogen, ppm          | 130    | 82          | 75       | 67           | 47          | 16          |
| Oxygen, wt%            | 0.0    | 1.2         | 1.2      | 1.1          | 4.7         | 8.9         |
| Aromatics, wt%         |        |             |          |              |             |             |
| Mono                   | 17.76  | 15.85       | 15.87    | 15.86        | 10.32       | 3.34        |
| Di                     | 7.39   | 6.60        | 6.60     | 6.60         | 4.29        | 1.39        |
| Poly                   | 2.1    | 1.87        | 1.88     | 1.87         | 1.22        | 0.39        |
| Total                  | 27.25  | 24.32       | 24.34    | 24.33        | 15.84       | 5.12        |
| D2887 Distillation,°F  |        |             |          |              |             |             |
| IBP                    | 222    | 209         | 209      | 210          | 239         | 329         |
| 10%                    | 477    | 465         | 459      | 465          | 498         | 571         |
| 30%                    | 579    | 559         | 557      | 559          | 579         | 1009        |
| 50%                    | 613    | 595         | 592      | 594          | 631         | 1119        |
| 70%                    | 643    | 632         | 628      | 630          | 1108        | 1130        |
| 90%                    | 681    | 720         | 688      | 715          | 1130        | 1135        |
| FBP                    | 740    | 1127        | 1121     | 1127         | 1134        | 1139        |
| Cloud Point,°F         | 19.9   | 21.7        | 24.1     | 22.8         | 22.0        | 19.1        |
| Cetane Index           | 53.8   | 50.6        | 51.2     | 50.9         | 46.4        | NA          |

Table 3. Straight-Run (SR) and Bio-Blend Analyses

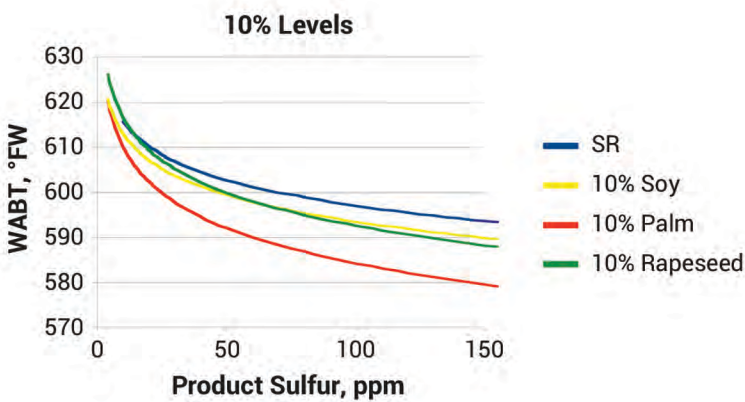


Figure 6. Results of Various Renewable Components

Looking at other diesel product properties that are important to refiners reveals that there is a boost in the product cetane index by almost 2 numbers. This increase in cetane was seen over the wide range of conditions tested and is a reflection of the normal paraffins from the renewable oil discussed above.

Figure 7 summarizes some of the cetane index results achieved at higher pressure for each of the bio-feed blends.

The impact of low pressure operation on cetane improvement is shown in Figure 8 for a 10% renewable feed blend. Not surprisingly, lower pressure operation results in a lower cetane index for the SR feed, but the addition of the renewable oil again provides a consistent two number increase in cetane index.

This is a good indicator that the large fatty acid molecules are being broken down into the three individual fatty acid chains via the breaking of the C-O bonds. Figure 9 compares the D-2887 distillation chromatograms of the SR products at 10 ppm sulfur to that of the coprocessed products, and it is evident that there is an increase in the concentration of the n-paraffins between 500°F and 600°F boiling points. It is this increase that yields the significant boost in cetane.

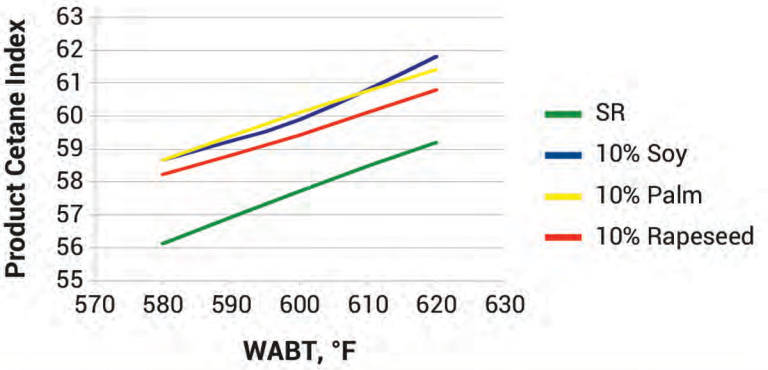


Figure 7. Cetane Boost when Co-Processing Bio-Feeds at High Pressure

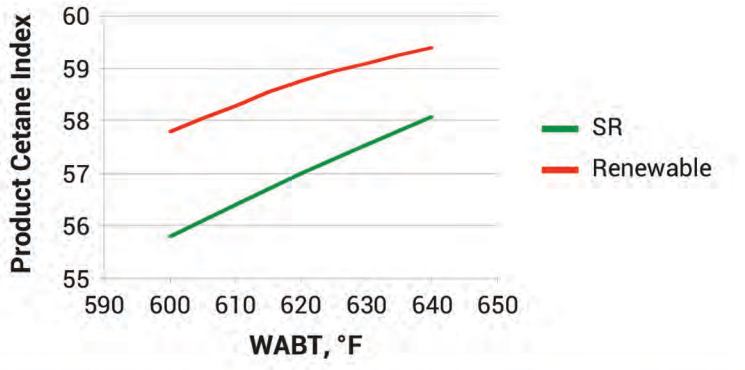
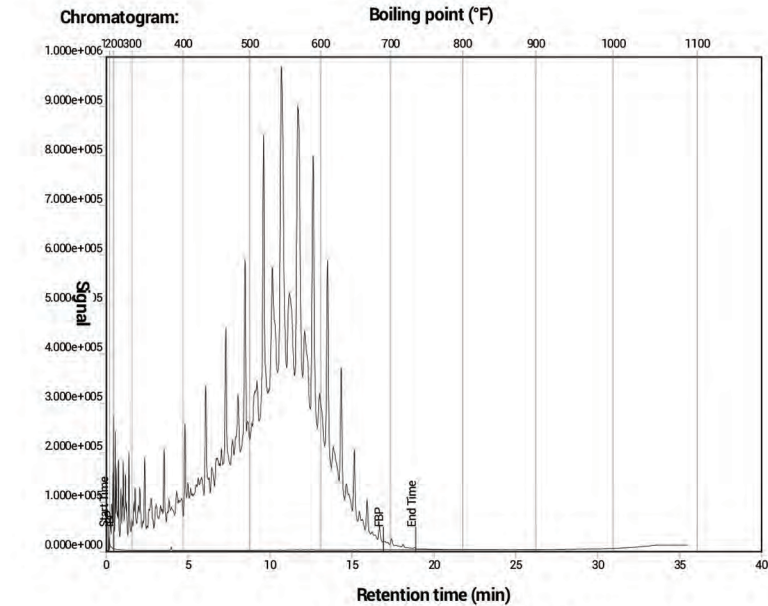
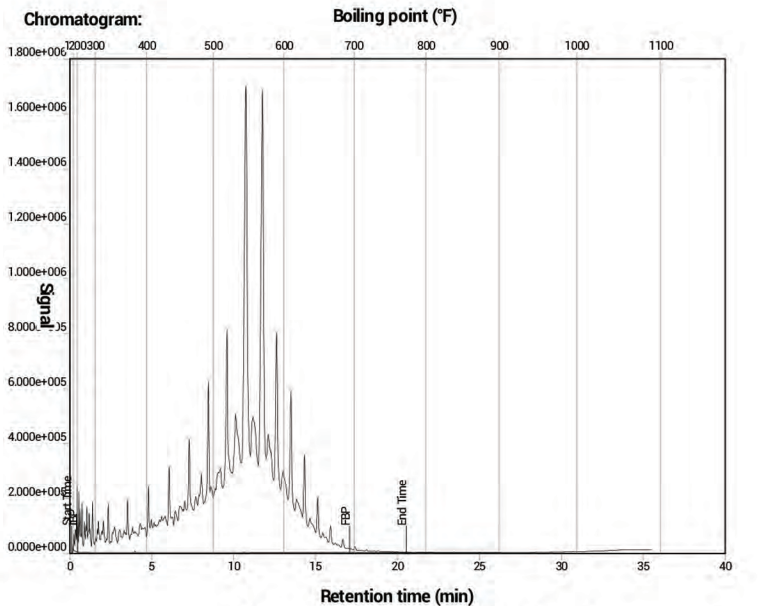


Figure 8. Cetane Boost when Co-Processing Bio-Feeds at Low Pressure



Straight-run product  
@ 10 ppm sulfur



Co-processed product  
@ 10 ppm sulfur

Figure 9. Results of Various Renewable Components

The hydrotreating of the bio-blended oil results in a product that no longer contains material in the C<sub>50</sub> to C<sub>60</sub> range. This is consistent with the theory that the individual fatty acid chains are being broken apart to hydrocarbons of similar size to those in the SR diesel.

Due to the addition of unsaturated chains from the bio component, there is expected to be an increase in hydrogen consumption to saturate these C=C bonds. With this additional hydrogen usage, it is important to also be aware of any changes in product aromatics, as reactions to saturate aromatics are high consumers of hydrogen and would compete with the saturation reactions under hydrogen limited conditions. Figure 10 summarizes the product aromatics for one of the bio-blended feeds. The total aromatics are consistently two

numbers lower than the SR feed, which is the same as the actual difference in the total aromatic content of the two feeds. The lower aromatic content of bio-blended feeds allows the refiner to achieve lower product aromatic content, which may be valuable as future regulations may require a lower total aromatic limit on diesel fuel.

At lower pressure and H<sub>2</sub>/oil ratios, the total aromatic content shows a similar response, with two numbers lower total aromatics when co-processing bio-based feedstock. With reduced operating pressure, there is a decrease in the aromatic saturation ability of the catalyst, and the possible use of renewable oils may help to offset this.

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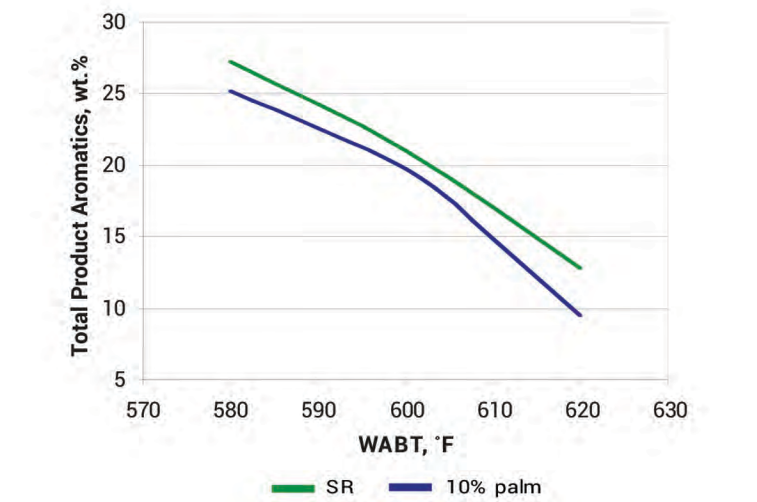


Figure 10. Comparison of Total Aromatics of SR Oil with 10% Renewable Oil at High Pressure

Cloud point specifications vary based on the location of the refinery and the end user of the fuel. Although the blending of the bio components yields improvements in the diesel cetane, there is the concern about the biofeed based diesel cloud point. It is widely known that n-paraffins have a significantly higher cloud point than other same carbon number hydrocarbons. Since hydrotreating converts the fatty acid chains into long chained n-paraffins, the cloud point of the mixture will increase. Figure 11 summarizes the product cloud points after hydrotreating the three blended feeds. The SR feed is included for comparison.

Processing the SR feed has essentially no impact on the product cloud point and the products are all within a few degrees of the feed cloud point shown in Table 3. The renewable containing feeds all have slightly higher cloud points compared to the SR feed (see Table 3), and after hydrotreating the cloud point increases by 6 to 10°F. This increase in cloud point can be significant especially in cold weather climates. By using other technology provided by ART, the problem of increased cloud point can be reduced or eliminated.

Co-Processing in FCC Units

Another option for refiners could be to co-process bio components in fluid catalytic cracking units (FCCUs). Unlike hydrotreater units where catalyst cannot be changed without taking the unit out of service to reload the reactor, continuous replacement of catalyst in the FCC unit enables the refiner to adjust the catalyst formulation to optimize yields. Characterization of the biofeedstock and an understanding of the refiner's objectives can allow the catalyst supplier to develop a formulation to maximize profits.

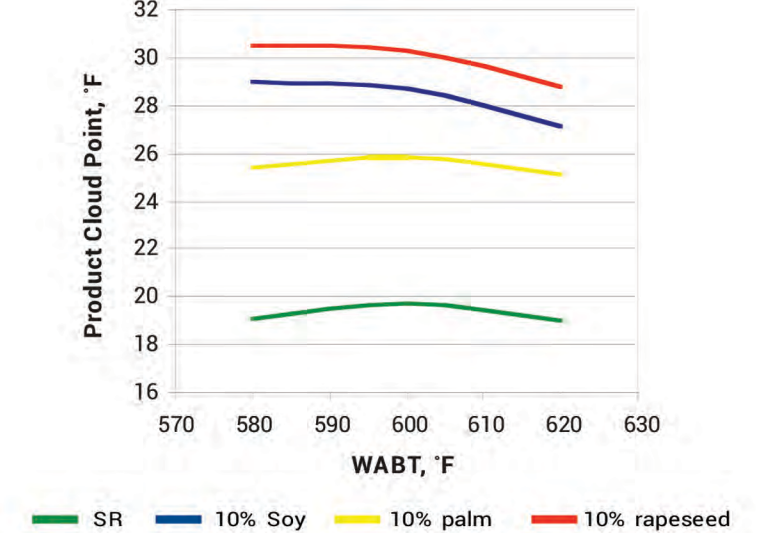


Figure 11. Cloud Points of Bio-Blended Feeds Compared to SR Feed

Pilot Plant Testing of Renewable Oils

To illustrate the impact on FCC yields with the incorporation of vegetable oil feedstocks into FCC feed, a pilot plant study was conducted by starting with a composite feed of VGO and resid with properties shown in Table 4, then the soybean, palm and rapeseed oils used in the hydrotreating testing were blended to 0%, 7.5% and 15% concentrations. The hydrotreated VGO in this table is used in a later study to compare the effects of different base feedstocks.

The blended FCC feeds were cracked over an FCC catalyst, which was deactivated using a CPS-3 type protocol<sup>3,4</sup> to 1000 ppm nickel and 2000 ppm vanadium. The catalyst was formulated to provide maximum bottoms upgrading. Properties of the deactivated catalyst are shown in Table 5.

The pilot unit was run at a constant reactor temperature of 1000°F, and the deactivated catalyst was tested at three catalyst-to-oil ratios (4,6,8) for each of the blended feeds in the pilot unit.

Figure 12 shows that all three of the blended bio-feeds are easier to crack than the base feed. The addition of the bio component increases the cracking activity (lower cat to oil for a given conversion), and increasing the concentration of a given bio component yields an increase in conversion at constant cat to oil ratio.

Figure 12. Conversion vs. Cat to Oil

|                           | Composite Resid | Hydrotreated VGO |
|---------------------------|-----------------|------------------|
| API                       | 24.4            | 27.3             |
| Sulfur, wt%               | 0.53            | 0.20             |
| Nitrogen Total/Basic, ppm | 813/287         | 800/280          |
| Concarbon, wt%            | 1.12            | 0.2              |
| K-Factor                  | 11.96           | 12.23            |
| Aromatic Ring, wt%        | 22.7            | 18.9             |
| Naphthenic Ring, wt%      | 13.6            | 11.5             |
| Paraffinic Carbons, wt%   | 63.8            | 69.5             |
| Vanadium, ppm             | 2.5             | 1.8              |
| Nickel, ppm               | 1.1             | 0.7              |
| D6352 Distillation,°F     |                 |                  |
| IBP                       | 494             | 460              |
| 10                        | 689             | 703              |
| 30                        | 775             | 786              |
| 50                        | 834             | 849              |
| 70                        | 899             | 923              |
| 90                        | 1018            | 1034             |
| 95                        | 1110            | 1088             |
| FBP                       | 1279            | 1226             |

Table 4. Feedstock Analysis for FCC Study

| MAT, wt%              |       |
|-----------------------|-------|
| Total Surface, m²/g   | 175   |
| Zeolite Surface, m²/g | 99    |
| Matrix Surface, m²/g  | 76    |
| Unit Cell Size, Å     | 24.29 |
| Rare Earth, wt%       | 2.04  |
| Alumina, wt%          | 50.23 |

Table 5. Deactivated Catalyst Properties

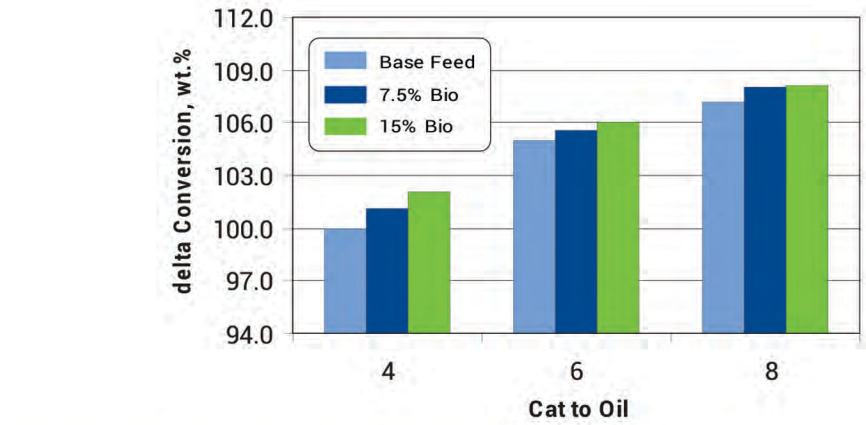


Figure 12. Conversion vs. Cat to Oil

Figure 13 shows that the bio-feeds produce significantly less coke per unit conversion than the base feed. Increasing the concentration of any of the three bio components further reduces the amount of coke produced for a given conversion. The rapeseed oil is the easiest to crack, followed by the soybean oil with the palm oil being the most difficult of the components to crack.

The trends observed in Figures 12 and 13 can be explained by the individual fatty acid compositions for each of the bio components reported previously in Table 1. The reaction pathways for triglycerides have been studied extensively by Dupain et. al.<sup>5</sup>, and under FCC conditions, were found to occur in two distinct steps. First, thermal cracking of the triglyceride occurs, releasing the fatty acid chains from the glycerin backbone. Conversion of free fatty acids via thermal cracking is very low, requiring catalytic cracking in the subsequent step to break the high molecular weight fatty acid molecules into smaller, more valuable products. Free fatty acids with more saturation will be more difficult to crack than those that contain greater amounts of double bonds<sup>6</sup>. With the lowest average of 1.1 double bonds per fatty acid chain, this explains the performance of the palm oil versus the soy or rapeseed oils.

The bio-feeds also have significantly less contaminants (sulfur, nitrogen, and potentially metals) than the base feed, but additional characterization of these materials is very difficult. Traditional analysis methods developed for fossil based hydrocarbons will not apply to the bio-based materials. Measurements such as concarbon, n-d-M (which is an estimate of the chemical composition of the feedstock using refractive index (n), the density (d) and the molecular weight (M) of the feed to calculate the amount of paraffinic (Cp), naphthenic (Cn), and aromatic (Ca) carbon species in the feed) and even GC based distillations can be flawed due to the thermal cracking

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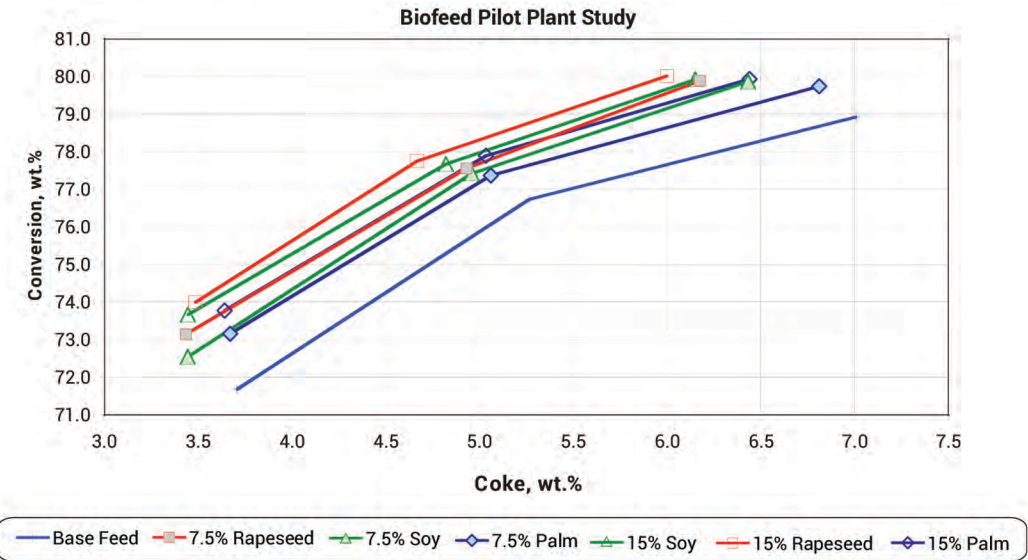


Figure 13. Conversion vs. Coke

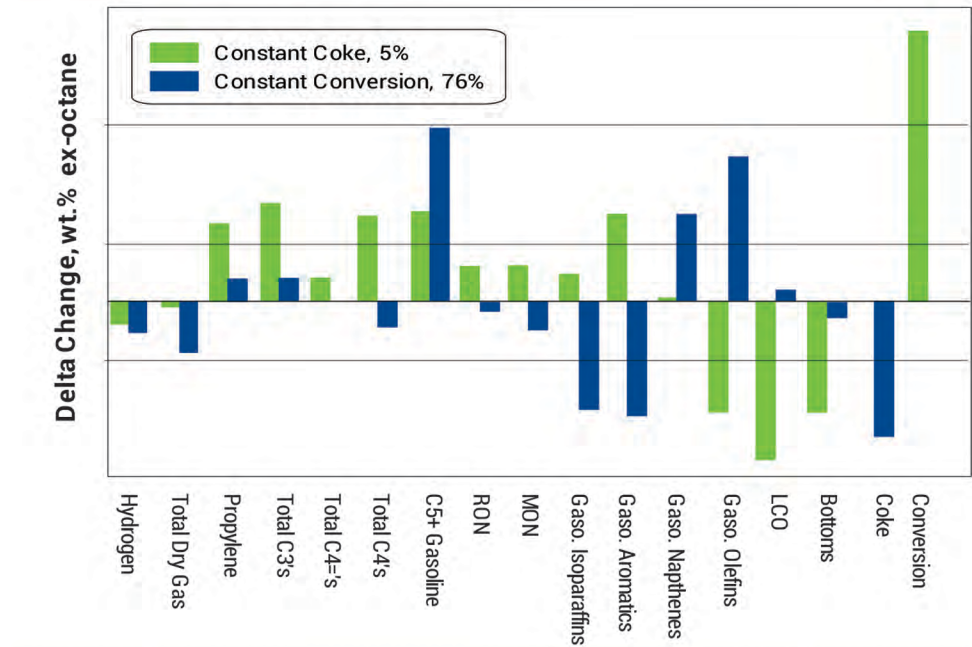


Figure 14. Comparison of 15% Blended Feeds

response of the bio-feeds. With virtually no sulfur in each of the bio-feeds, incorporating them into FCC feed would dilute key FCC product stream sulfur levels, potentially allowing for downstream hydrotreating benefits (less gasoline octane loss, extended catalyst run length) or for a lower cost base FCC feed at constant product sulfur.

Since the increase in the concentration of the biofeeds in the feed directionally increases the magnitude of the response in the FCC yields, to simplify the trends the remaining results will be presented for only 15% blends. Additionally, while commercial FCC units operate to constant coke, if there is a significant difference in coke yield when comparing individual product yields, the constant coke comparison will accentuate the

differences in yields. Comparing data on a constant conversion basis will smooth out the data and allow for a more representative comparison. Figure 14 shows the yields for the biofeeds at 15% concentration for constant coke and conversion compared to the base feed.

Beginning with hydrogen, Figure 15 confirms that the reduction in hydrogen yield with the biofeeds is significant. Hydrogen can come from three sources: a by-product of dehydrogenation with metals, a product of thermal cracking, or a product of catalytic cracking.

One potential method to determine the reason for the reduction in hydrogen with the bio-based materials involves a comparison of the C<sub>5</sub> olefins yields in gasoline for the feeds tested. During dehydrogenation reactions, gasoline range olefins react with the metals on the catalyst to produce hydrogen<sup>7</sup>. If the biofeed materials produce less gasoline range olefins than the base feed, this could be the cause for the reduction in hydrogen.

From our analysis, the addition of biofeeds to the base feed does not reduce the amount of gasoline olefins produced, and therefore the reduction in hydrogen observed with the biofeeds is not likely due to reduced dehydrogenation reactions.

Alternatively, the potential for the biofeeds to produce hydrogen during the catalytic cracking process can be evaluated by comparing the propane yield for the feeds tested. In cracking a biofeed, the fatty acid molecules that were liberated by the initial thermal cracking step will subsequently crack along the pathways defined for either paraffin or olefin molecules. If the fatty acid mixture is more olefinic, it will be very reactive and will easily crack to produce smaller gasoline range olefins<sup>6</sup>. A more paraffinic fatty acid mixture can react along multiple potential pathways to produce a variety of products (Figure 16).

The initiation step occurs on either Bronsted or Lewis acid sites on the catalyst, and on the Bronsted site there

are two additional potential pathways for the paraffin to react to produce a carbenium ion. Protolytic cracking can occur with the elimination of the paraffin,

or the carbenium ion can be formed with the elimination of a hydrogen molecule (Figure 17).

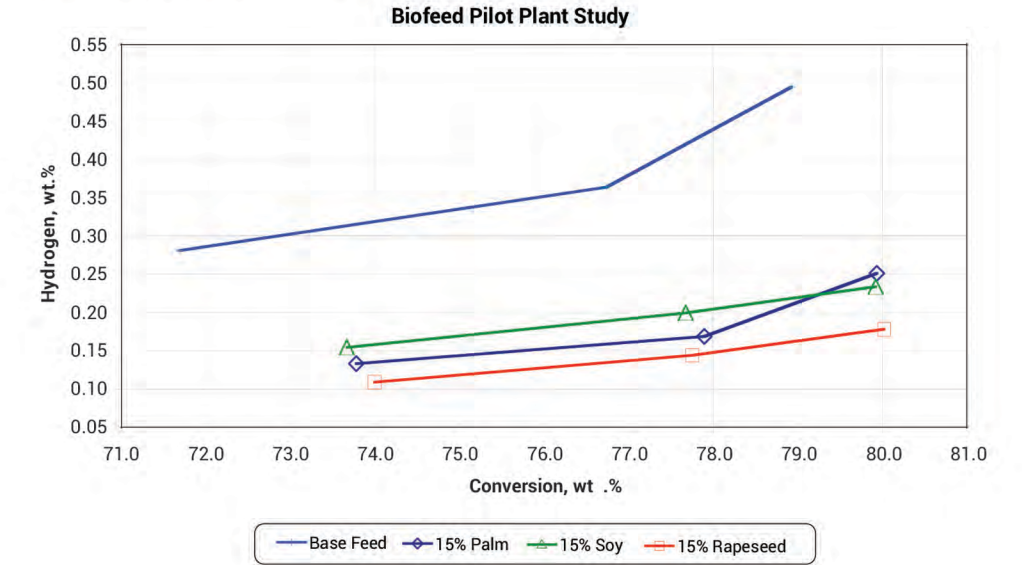


Figure 15. Hydrogen Yield vs. Conversion

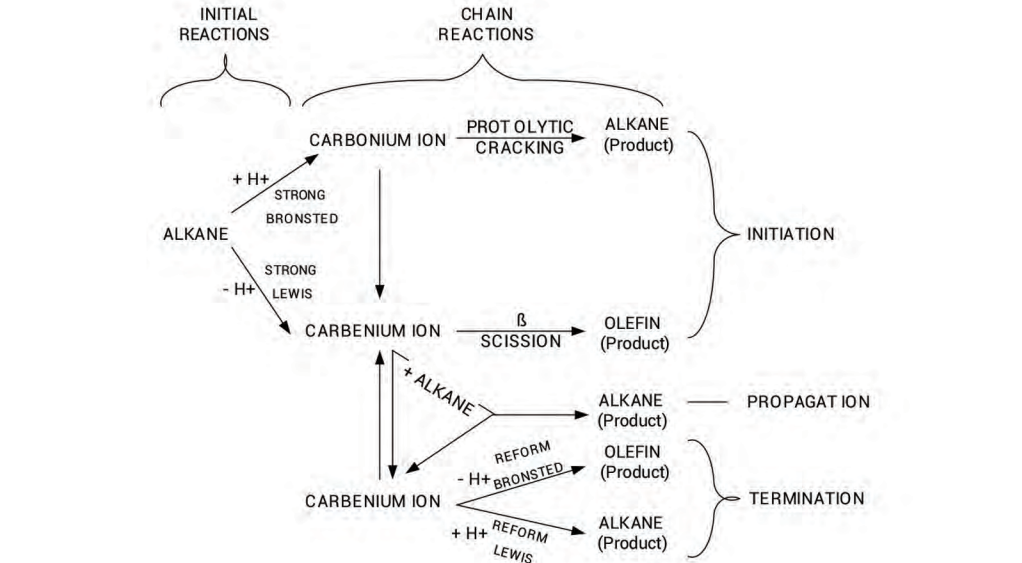


Figure 16. Reaction Pathway Network for Alkane Cracking

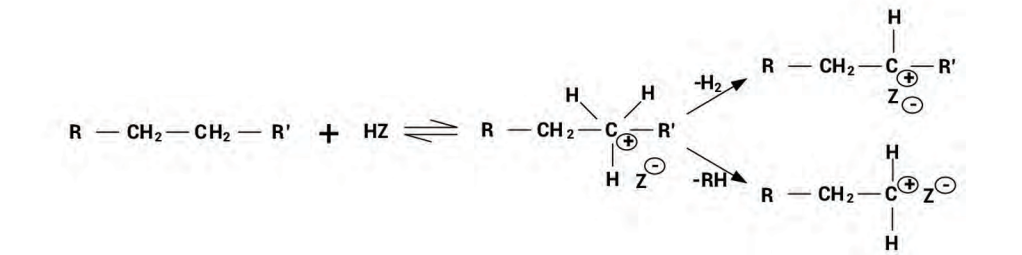


Figure 17. Paraffin Reaction Pathway

If protolytic cracking is prevalent, the chain terminating product is propane. Figure 18 shows that the propane yield for all three of the biofeeds is lower than the base feed. Thus there is an indication that the reduction in propane and hydrogen is potentially due to reduced protolytic cracking of the fatty acids compared to a typical FCC feed. This also indicates that the double bonds on each of the free fatty acid molecules, which are more reactive, are the initiation sites for the cracking reactions.

The fatty acid molecules are cracking into gasoline and propylene, as can be seen in Figures 19 and 20.

The gasoline trend indicates overcracking for all three of the biofeeds, and also for the base feed. Over cracking occurs when the gasoline molecules produced are subsequently cracked into lighter molecules. Catalyst activity, cat to oil ratio, and temperature can all drive a feed to over-cracking, and the easier the feed is to crack, the higher the tendency to over-crack. Table 4 shows that the base feed itself is fairly paraffinic, with a Watson K-Factor that indicates it will produce high conversions. The incorporation of the highly paraffinic fatty acids from the biofeeds makes the blended feeds even easier to crack. Catalyst activity will be determined based on specific unit constraints and objectives when commercial processing of the blended bio-containing feeds. The overcracking trends observed in the pilot plant testing can be corrected and is not expected in commercial operations.

The influence of the bio-based materials on the gasoline properties is important, as the oxygen species in the triglycerides could break down to water, or they could potentially be converted into aldehyde and furan species which are undesirable from an environmental, health and safety perspective. Gas Chromatography-Atomic Emission Detector (GC-AED) was performed on the liquid product, which was recovered after each test run through the pilot unit.

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The GC-AED was run in oxygen mode in order to detect oxygen species using the same technique as in Figure 4 and 5. The only peaks that showed up were initial peaks between two and four minutes from the syringe wash solvents. No discernible oxygen peaks were present in the liquid product thus, no undesirable oxygen species were present.

The (R+M)/2 octane of the gasoline produced by the biofeeds is lower than the base feed, with contributions from both RON and MON contributing to the trend. The magnitude of the response in gasoline RON may depend on the source of the biofeed, but in general the loss of RON is fairly small. (Figure 21) MON is consistently lower with the biofeeds, and this is due to the lower aromatics content of the gasoline produced with the biobased materials in the feed.

The response in C<sub>4</sub> yields can be explained by again reviewing the individual fatty acid compositions for the three biofeeds as shown earlier. Palm oil contains significant percentages of both C<sub>16</sub> (palmitic) and C<sub>18</sub> (oleic) acids. The highest % fatty acid in soybean oil is C<sub>18</sub> (linoleic), and C<sub>20</sub> and C<sub>22</sub> (arachidonic and erucic) acids are present in the largest concentrations in rapeseed oil. Once these molecules are liberated from the glycerin backbone via thermal cracking, they follow a typical FCC rule of thumb, which is that the longer the chain (ie. the higher the carbon number in the molecule), the more broad the distribution of product olefins that will result from catalytic cracking of the molecule. Thus, the palm oil produces the largest amount of C<sub>4</sub> olefins, as seen in Figure 22.

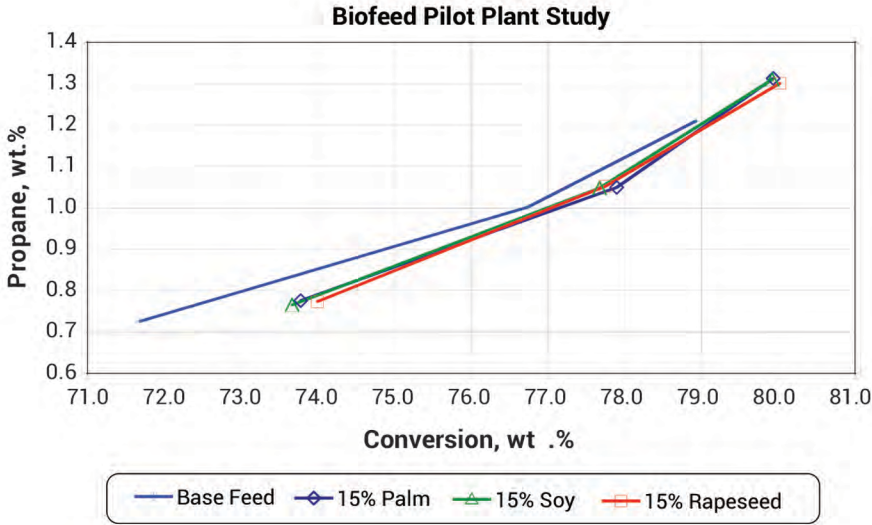


Figure 18. Propane Yield vs. Conversion

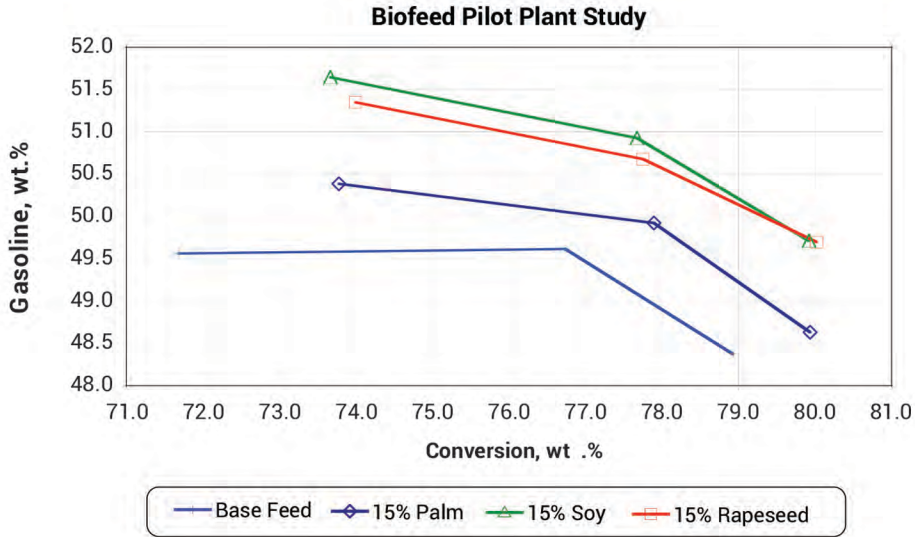


Figure 19. Gasoline Yield vs. Conversion

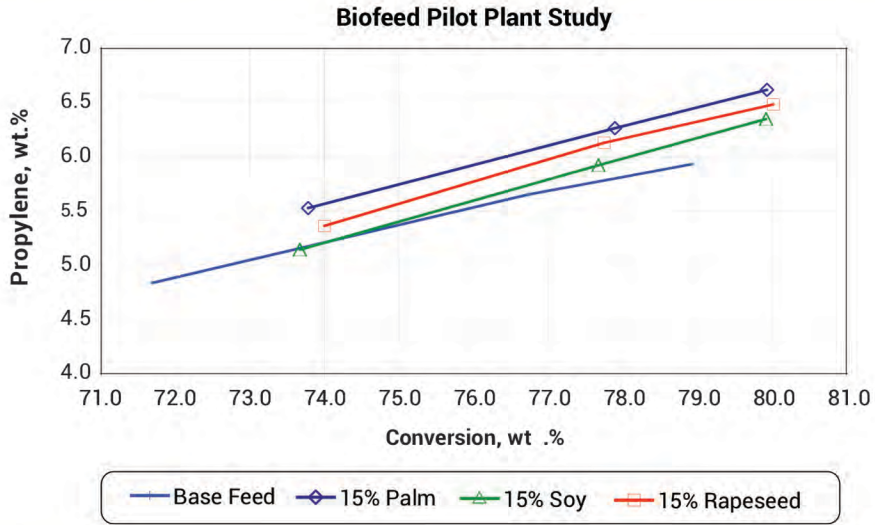


Figure 20. Propylene Yield vs. Conversion

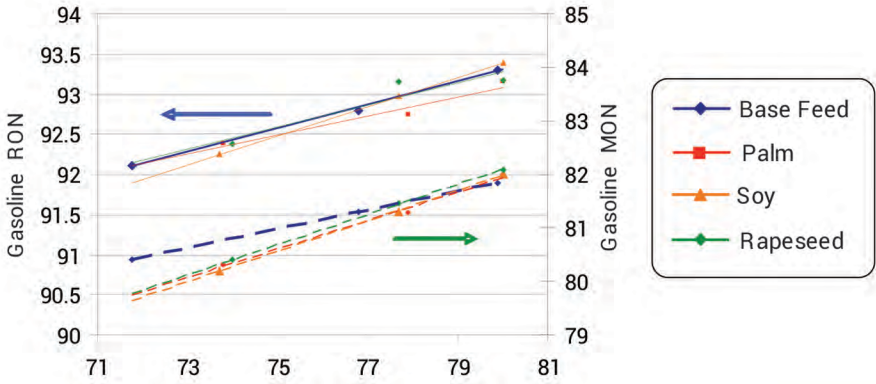


Figure 21. Gasoline RON & MON for Bio-blends

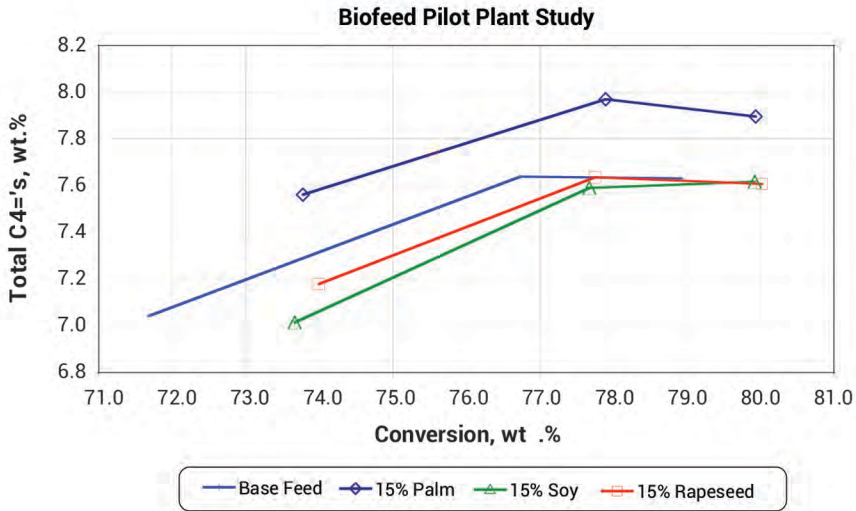


Figure 22. Butylene Yield vs. Conversion

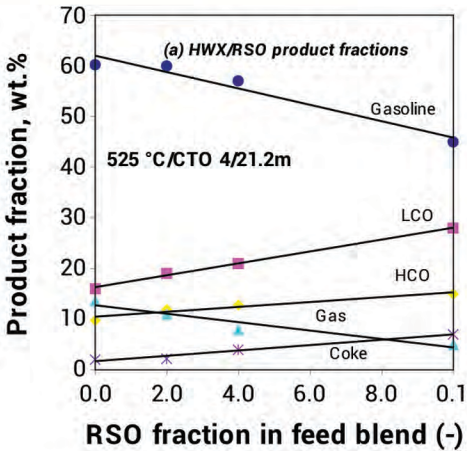
Influence of Base Properties

Ultimately the yield response for the addition of a bio-feed material into FCC feed will depend on the properties of the base FCC feed. Dupain et al.<sup>5</sup> observed that the addition of rapeseed oil to a hydrowax feed would yield less gasoline and C4 minus products, and higher amounts of LCO, slurry and coke (Figure 23).

While the properties of the specific hydrowax feed are not known, in general these feeds are highly paraffinic and the addition of vegetable oils to that type of feed would in fact degrade the overall properties of the feed. This is confirmed by comparing the response in yields for the addition of rapeseed oil to the two base FCC feeds from Table 4. The general trends in yields for constant conversion

are shown in Figure 24. The addition of rapeseed oil to the hydrotreated VGO feed produced more coke and hydrogen, at constant conversion, but at constant coke the conversion was actually lower with the rapeseed oil in the feed. By comparison, the composite feed shows strong improvements in yields with the addition of rapeseed.

These trends suggest that if a base FCC feed is paraffinic, yields may in fact worsen with the addition of a bio based material into the feed, whereas for VGO or resid types of feed, yields may instead improve. Future work will include examining the role of the base feed on yields with the incorporation of biofeed materials into the FCC feed.



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Figure 23. Quantitative Yields for Different Hydrowax/Rapeseed Oil Blends

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Continued from Page 30

|          | Hydrotreated VGO | Composite Feed |
|----------|------------------|----------------|
| Hydrogen | ↑                | ↓              |
| Wet Gas  | ↓                | ↑              |
| Gasoline | ↑                | ↑              |
| LCO      | ↓                | ↓              |
| Bottoms  | ↓                | ↓              |
| Coke     | ↑                | ↓              |

**Red:** Undesirable

**Green:** Undesirable

**Grey:** Depends on the refiners objectives and constraints

Figure 24. Yield Trend Comparison for Feeds at Constant Conversion

Conclusion

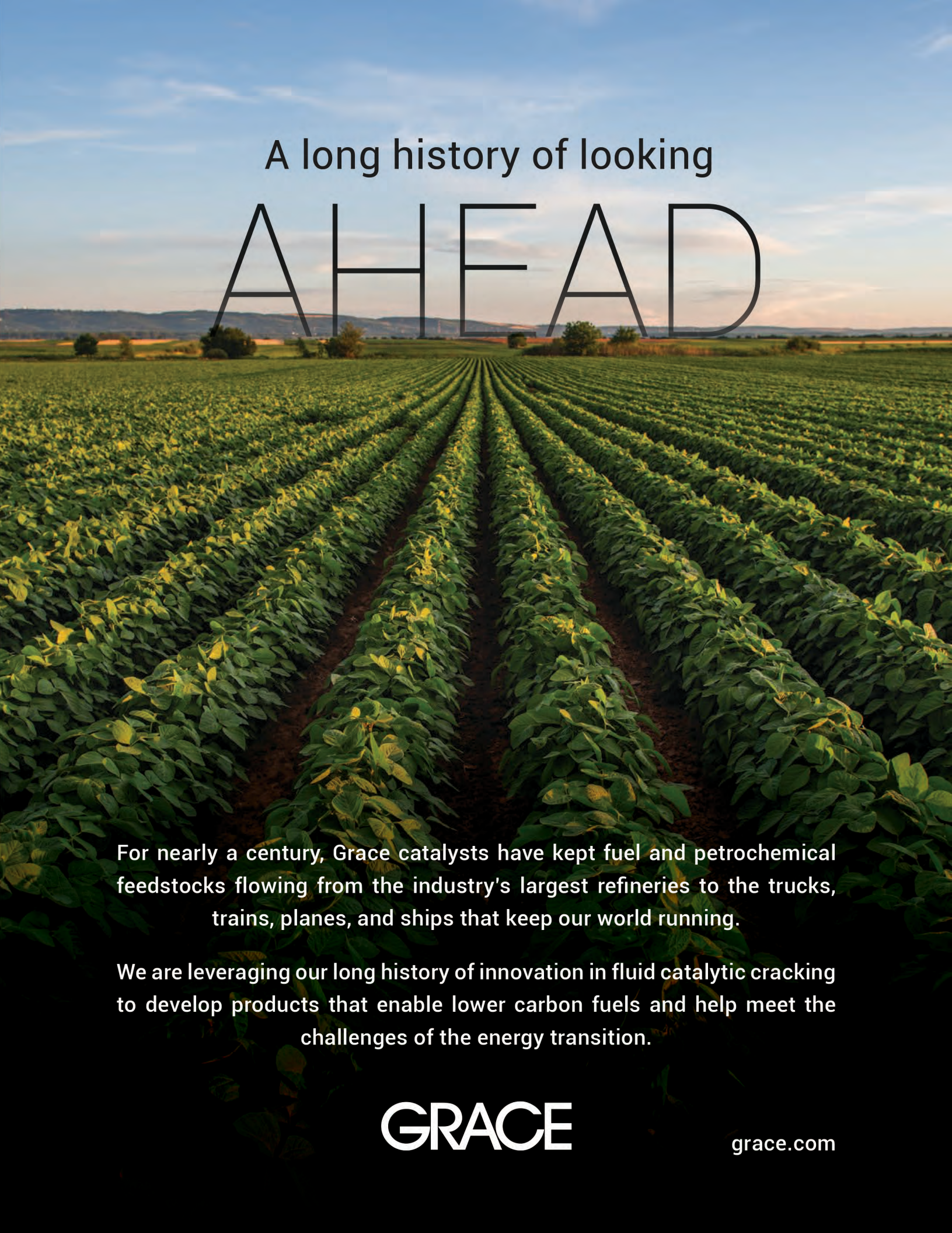
Based on these results, the use of ART’s high activity hydroprocessing catalysts or Grace’s high performance FCC catalysts can enable refiners to co-process renewable oils through conventional refining equipment. Co-processing can be incorporated into a refiner’s operating strategy with minimal detriment to catalyst stability or yields, but the effect on an individual operation will depend on the base feed and conditions. Grace Davison’s Biofuel Technologies Group utilizes resources across Grace and its affiliates to evaluate options for refiners who wish to consider incorporating co-processing biofeeds into their operation, but want to understand the optimum configuration to maximize their profitability.

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Susan Ehrlich, Business Director Biofuel Technologies Group;  
Rick Wormsbecher, Research and Development Fellow, Refining Technologies

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