Refining biofeedstock innovations

Analysis of processing routes for producing renewable diesel, gasoline and olefins with feedstocks that include vegetable oil, pyrolysis oil and biomass. Biorenewable integration in refineries is evaluated along with work to commercially produce green diesel.

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UOP-Honeywell

The production of renewable fuels has been expanding worldwide, driven by increasing petroleum prices, government mandates and incentives, as well as commitments to Green House Gas reduction. Despite this growth in renewable fuels, there has been little integration of renewable fuels with petroleum refineries. This segregation of renewable fuel increases the cost of production, since it does not take advantage of any existing infrastructure for the production and distribution of fuels. Renewable fuels would find greater application in meeting the increasing demand for transportation fuels if economical opportunities for blending or co-processing in traditional petroleum refineries could be identified and developed.

In order to evaluate profitable refining
processing options for biologically derived feedstocks, UOP partnered with the US Department of Energy (DOE), the National Renewable Energy Laboratory (NREL), Pacific Northwest National Lab (PNNL) and Michigan Tech University (MTU) to commercialise a process to produce green diesel, a high-cetane fuel, from vegetable oil. During this study, options for integrating biorenewable feeds and fuels into existing refineries were identified.

Many options were found, including the production of liquid transport fuels through co-processing and standalone production plants. Processes to convert these feedstocks into chemicals, hydrogen and power production were also considered. Details of promising processing options were defined after completing proof-of-principle experiments in batch and continuous pilot plants with online analysis of products. The data were used to develop models and correlations to estimate commercial performance. From these estimates, the potential business value of biorenewable integration in conventional refineries was evaluated. Government subsidies were required to make some of the processes economically attractive, but several of the options were favourable without subsidies. All options become more attractive with high crude oil prices.

A schematic showing several options for biofuel production from different biomass sources is shown in Figure 1. Some of the routes are already in commercial practice, such as ethanol from the fermentation of corn or sugar cane, or biodiesel production from oils. Other less developed technology, such as the deoxygenation of plant oils to produce a green diesel fuel, will soon be a common renewable fuel. Several routes have a considerable longer time frame for commercialisation due to the technical challenges required for economic conversion to fuels.

**Biofuel and biofeedstock sources**

Figure 2 compares the global volume of petroleum-based liquid transport fuels and the current biofuels; bioethanol from starches and sugars; and biodiesel from vegetable oils. The potential supply of these fuels is small relative to the global demand for transportation fuels. About 13% of US corn production was used to supply ethanol for 2% of the US gasoline market in 2005. In addition, vegetable oils and greases could only replace a very small fraction of transportation fuel. The large supply of lignocellulosic biomass could supply a high percentage of future liquid transport fuels if commercial processes were available to convert these feeds. One such process evaluated in this study was fast pyrolysis. The quantity of pyrolysis oil is currently very low, since there is little commercial production due to a lack of demand.

The study took into account both feedstock costs and the projected prices of potential products. Current prices of raw vegetable oils, greases and pyrolysis oils were used in the economic assessment. The costs ranged from $16/bbl for pyrolysis oil to greater than $75/bbl for raw vegetable oils. Each economic analysis was based on a West Texas Intermediate (WTI) crude price of $40 per barrel, a level considerably lower than the recent greater than $60/bbl price. The cost of each potential biofuel was compared to this crude price after incorporating a number of factors that included capital costs, transportation costs, CO2 credits, subsidies, and cetane and octane numbers. Most of the feedstocks looked promising when current US subsidies were applied.
Several were economically attractive without subsidies. Vegetable oils were not attractive without subsidies until crude prices exceeded $70/bbl.

The properties of biorenewable feedstocks were compared to petroleum, as shown in Table 1. The biggest difference between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels ranging from 10–40%. Petroleum has essentially none. These feedstocks are often more polar, and some easily entrain water and can therefore be acidic. All have very low sulphur levels and many have low nitrogen levels, depending on their amino acid content. Bio-derived feedstocks are incompatible with typical refinery operations due to the acidity and alkali content, so processes were identified to pretreat many of these feeds before entering refinery operations.

Opportunities for vegetable oils and greases
Options were identified for processing vegetable oils and greases in refineries, as shown in Figure 3. One option is to produce gasoline or olefins in an FCC unit. These oils could also be deoxygenated using hydroprocessing technology to produce a high-cetane green diesel product. Different fits for the production of biodiesel in refineries were also evaluated.

Catalytic cracking of vegetable oils and greases was identified, and one example is shown in Figure 4. A pretreatment unit is required to remove catalytic poisons such as alkali metals and other problem components such as water and solids. The pretreated feed can then be introduced as a co-feed with virgin gas oil (VGO) to produce gasoline and other products. A modified catalytic cracking process can produce high-value products such as ethylene and propylene.

Estimated yields for each processing option are shown in Tables 2 and 3, which compare standalone processing of the vegetable oils to VGO. Co-processing experiments are in progress. Vegetable oil and greases produce gasoline yields similar to VGO, with reduced yields of heavier and often undesirable products such as light cycle oil (LCO) and clarified slurry oil (CSO). Such processing also produces a significant amount of water and/or CO₂ as a consequence of feedstock deoxygenation in the FCCU. Results were similar for olefins production, where vegetable oil and greases can produce competitive yields of ethylene and propylene with reduced amounts of gasoline, LCO, and CSO. RON values are slightly higher for processing vegetable oils in both catalytic cracking schemes, while coke yields are slightly higher for gasoline production. In either case, the use of vegetable oils and greases in catalytic cracking units is feasible.

Green diesel production
The use of existing hydroprocessing technology was evaluated for the deoxygenation of vegetable oils and greases to produce a paraffinic diesel fuel through two promising processing options. As with catalytic cracking, co-processing in existing units requires a pretreatment unit to remove alkali metals and hydrogenate units of unsaturation on the fatty acid chains. The pretreated feed is then fed to an existing hydrotreater. We prefer to produce the green diesel in a separate unit, where processing conditions are optimised for the vegetable-oil-based feedstock. FCC processing in a modular unit is not feasible, since these units are not readily scaled down. This modular green diesel unit could be constructed at an existing refinery or at a remote location. The paraffinic product could be blended with the hydrotreated diesel or could serve as a high-quality diesel fuel on its own.

This modular approach is attractive for feedstocks containing high percentages of free fatty acids or when transportation of the feedstock is prohibitively high, since construction near the feedstock source and the choice of proper metallurgy will solve both these issues. Generally, separate processing in a modular unit has the following advantages:

— Optimisation of the processing conditions and catalyst for conversion of the biofeedstock
— Minimisation of the use of...
expensive metallurgy for acidic biofeedstocks and products — Removal of products such as CO, CO₂ and H₂O, which impact the hydroprocessing catalyst — These factors must be weighed against the advantage of using existing processing capacity, particularly if it is underutilised.

Performance estimates for a green diesel process are shown in Table 4. Hydrogen requirements are variable, depending on both the degrees of unsaturation on the fatty acid chains and the deoxygenation mechanism, which itself depends on the choice of catalyst and processing conditions. Hydrodeoxygenation produces water and requires one hydrogen molecule for each oxygen removed, while decarboxylation removes one carbon to produce CO or CO₂. Breaking the triglyceride backbone produces propane or lighter hydrocarbons. The yield of a high-cetane and low-sulphur content green diesel product is greater than 98% on a volumetric basis.

Green diesel is an oxygen-free paraffinic feed and has several advantages over biodiesel, also produced from vegetable oil, as shown in Table 5. Green diesel is a high-cetane, straight-chain paraffin whose cold-flow properties can be adjusted by the appropriate level of isomerisation. The product cetane number can reach as high as 80–90. Biodiesel, a fatty acid methyl ester (FAME), is made by adding methanol to vegetable oils. FAME contains a significant amount of oxygen that lowers its heating value and contributes to higher NOx emissions for concentrated blends. There are some other differences in product properties not identified in the table. The production of FAME yields a significant amount of contaminated glycerol byproduct, while green diesel produces light hydrocarbons from the triglyceride backbone. The production of biodiesel requires a less flexible range of vegetable oil feedstock, and fatty acids must be removed prior to transesterification. Highly unsaturated fatty acids chains result in a less stable biodiesel product, since oxidation occurs at the double bonds when stored for extended periods of time. Green diesel has several property advantages over biodiesel and will likely be preferred by vehicle manufacturers.

Green diesel technology development has already been completed and a unit is planned for operation in a European refinery in early 2009. UOP is currently licensing this technology.

Figure 5 summarises the economic analysis of biofuels and chemicals production from oils and greases, comparing the NPVs of four products as a function of biofuels feedstock. The NPVs were ten-year NPVs with product pricing of diesel, gasoline and olefins produced from $40/bbl crude. The different bars represent different renewable feedstocks, including subsidised and unsubsidised soy. As can be seen, the subsidies have a large impact on the economics of these processes.

Refining opportunities for pyrolysis oil

Fast pyrolysis is a thermochemical process with the potential to convert cellulosic biomass into liquid fuels and feeds. Large amounts of cellulosic biomass are available around the globe. Solid biomass feedstock is injected into a fluidised bed with high heat-transfer capability for short contact times, followed by quenching to condense a liquid bio-oil in 50–75% yields, with gas and char forming the balance. The bio-oil contains the thermally cracked products of the original cellulose, hemicellulose and lignin fractions present in the biomass. It also contains a high percentage of water, often as high as 30%.

Table 6 shows an estimated biofuel product distribution for hydروprocessed pyroyllic lignin bio-oil based on experimental results. These estimates were used as a basis for economic calculations. The naphtha and diesel are produced along with a large amount of

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**Table 4**

<table>
<thead>
<tr>
<th>Products</th>
<th>Vol% naphtha</th>
<th>Vol% diesel</th>
<th>ppm S</th>
<th>Cetane number</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAME</td>
<td>&lt;1–10%</td>
<td>88–98+%</td>
<td>&lt;10</td>
<td>80–100</td>
</tr>
</tbody>
</table>

**Table 5**

<table>
<thead>
<tr>
<th>Feed wt% bpd</th>
<th>Pyrolytic lignin</th>
<th>H₂</th>
<th>Lt ends</th>
<th>Naphtha</th>
<th>Diesel</th>
<th>Water, CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2250</td>
<td>4–5</td>
<td>15</td>
<td>30</td>
<td>8</td>
<td>51–52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products</th>
<th>Vol% naphtha</th>
<th>Vol% diesel</th>
<th>ppm S</th>
<th>Cetane number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel (FAME)</td>
<td>11</td>
<td>0.883</td>
<td>&lt;10 ppm</td>
<td>38</td>
</tr>
<tr>
<td>Green diesel</td>
<td>0</td>
<td>0.78</td>
<td>&lt;10 ppm</td>
<td>44</td>
</tr>
<tr>
<td>Cloud Point C</td>
<td>-5</td>
<td>340–355</td>
<td>265–320</td>
<td>50</td>
</tr>
<tr>
<td>Distillation 10–90% pt</td>
<td>30–52</td>
<td>51–52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cetane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure 5 NPV comparison of biofuels and chemicals 5,8,10,11
water and CO₂ due to water removal and deoxygenation. As with the vegetable oil, hydrogen consumption and the yield of CO/CO₂ will vary, depending on the mechanism of deoxygenation.

**Vegetable oil processing options**

A life cycle analysis (LCA) of the various vegetable oil processing routes was conducted at Michigan Technological University using the proprietary Simapro LCA program. LCA is a method to determine and compare the environmental impact of alternative products or processes from “cradle-to-grave”. In this case, the scope of the analysis was from extraction through combustion. For analysis purposes, it was assumed that all fuels have the same performance in transportation use. The primary focus of the analysis was on fossil energy consumption and emission of greenhouse gases, although other impact categories are included.

The results of the analysis are shown in Figure 6. In general, the green products have much lower total environmental impact scores than petroleum diesel, primarily because of significantly lower production of climate-active CO₂. Of the biofuels, green diesel and green gasoline (from the catalytic cracking of vegetable oil) have the lowest environmental impact and CO₂ production. The environmental impact of biodiesel production is higher due to the methanol requirement, which is produced from natural gas through an energy-intensive process with a strong environmental burden.

**Summary**

A number of opportunities were identified for the integration of biorenewable feedstocks and biofuels in petroleum refineries, particularly for two promising feedstocks:

— Vegetable oils/greases to produce green diesel, gasoline or chemicals
— Pyrolysis oil to produce green gasoline.

Vegetable oil can be processed in the short term using commercially available refining technology, but will be restricted to producing a small fraction of liquid transport fuels due to a limited amount of feedstock. Pyrolysis oil processing requires more commercial development and is also limited by the availability of pyrolysis oil, since commercial production is still in its infancy. In the long term, however, the focus must be on the effective utilisation of cellulosic biomass.

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“Vegetable oil can be processed in the short term using commercial refining technology, but will be restricted to producing a small fraction of liquid transport fuels due to a limited feedstock.”

Renewable Energy Laboratory, D Elliott from Pacific Northwest National Laboratory and D Shonnard from Michigan Technological University.

References
1 Aden A, Biodiesel Information for UOP, memorandum prepared for UOP by NREL, 2005.
5 Greene N, Growing energy: how biofuels can help end America’s oil dependence, NRDC, 2004.
11 Tyson K S, Oil and fat R&D, presentation by NREL to UOP, 2003.

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