Consider upgrading pyrolysis oils into renewable fuels

New research is identifying processing routes to convert cellulosic biomass into transportation fuels


To enable a sustained supply of biomass-based transportation fuels, the capability to process feedstocks outside the food chain must be developed. Significant industry efforts are underway to develop these new technologies, such as converting cellulosic wastes to ethanol.

An alternate route being pursued involves using a fast pyrolysis operation to generate pyrolysis oil (pyoil for short). Current efforts are focused on developing a thermochemical platform to convert pyoils to renewable gasoline, diesel and jet fuel. The fuels produced will be indistinguishable from their fossil fuel counterparts and, therefore, will be compatible with existing transport and distribution infrastructure.

Background. Biofuel production is expanding globally due to increasing petroleum prices, government mandates and incentives and commitments to reduce greenhouse gas (GHG) emissions. With today’s biofuels produced almost exclusively from food-based sources like sugar cane, corn and vegetable oils, we must remain mindful of challenges like scarce arable land and water resources, rising food prices and even irresponsible cultivation practices that could potentially raise GHG emissions. It’s important to consider that diversification of the entire US production of corn and soy to fuels will, at best, replace only about 15% of the current gasoline and diesel consumption.

With these challenges, there is a heightened need to develop viable alternate means to produce biofuels from nonfood sources. The future widespread and sustainable use of biofuels will rely on several issues:

- Identifying a large, consistent quantity of non-food based renewable feedstock
- Producing biofuels at costs competitive with other fuels
- Transporting the biobased feedstock or fuel to distribution centers
- Developing new technology to produce fuels from the unique composition of these highly oxygenated feedstocks

Goals. The goal is to identify profitable processing options by addressing these issues. Fig. 1 shows several options for biofuel production from different biomass sources. Some routes are already in commercial practice, such as ethanol from the fermentation of corn or sugar cane and production of biodiesel from vegetable oils. Others have a considerably longer timeframe for commercialization due to technical challenges or

**FIG. 1** Overview of possible processing schemes to yield transportation fuels based on renewable feedstocks.
Refining Developments

TABLE 1. Availability of biorenewable feedstocks in the US

<table>
<thead>
<tr>
<th>Biorenewable feedstock</th>
<th>Definition</th>
<th>Amount produced in the US, bpd</th>
<th>Amount available for fuel production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable oils</td>
<td>Soy, cottonseed, canola, peanut</td>
<td>194,000</td>
<td>33,500</td>
</tr>
<tr>
<td>Recycled products</td>
<td>Yellow grease, brown (trap) grease</td>
<td>51,700</td>
<td>33,800</td>
</tr>
<tr>
<td>Animal fats</td>
<td>Tallow, lard, fish oil</td>
<td>71,000</td>
<td>32,500</td>
</tr>
<tr>
<td>Pyrolysis oil</td>
<td>Made from pyrolysis of waste biomass (cellulosic)</td>
<td>1,500</td>
<td>750</td>
</tr>
</tbody>
</table>

Source: USDA-FAS and National Renderers Organization.

TABLE 2. Typical properties of petroleum and biorenewable feedstocks

<table>
<thead>
<tr>
<th></th>
<th>Crude typical</th>
<th>Resid</th>
<th>Pyrolysis oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, %</td>
<td>83 – 86</td>
<td>84.9</td>
<td>32 – 44</td>
</tr>
<tr>
<td>H, %</td>
<td>11 – 14</td>
<td>10.6</td>
<td>7.5 – 8.6</td>
</tr>
<tr>
<td>S, %</td>
<td>0 – 4 (1.8 avg)</td>
<td>4.2</td>
<td>0.2</td>
</tr>
<tr>
<td>N, %</td>
<td>0 – 1 (1 avg)</td>
<td>.3</td>
<td>0.1 – 0.7</td>
</tr>
<tr>
<td>O, %</td>
<td>—</td>
<td>—</td>
<td>44 – 55</td>
</tr>
<tr>
<td>H/C</td>
<td>1.8 – 1.9</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Density</td>
<td>.86 (avg)</td>
<td>1.05</td>
<td>1.17</td>
</tr>
<tr>
<td>TAN</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&gt;100</td>
</tr>
<tr>
<td>ppm alkali metals</td>
<td>60</td>
<td>6</td>
<td>100</td>
</tr>
<tr>
<td>Heating value, Btu</td>
<td>41,800</td>
<td>40,700</td>
<td>15,200</td>
</tr>
</tbody>
</table>

Feedstock availability. The processing route for producing biofuels from forest and agro-wastes by first converting to pyrolysis oil and then upgrading to transport fuels is the focus of this article.

Study basis and methodology. The first question addressed was the availability of biorenewable feedstocks based on 2005 data. Table 1 shows the US availability of several biofeedstocks. It is evident that vegetable oils and greases could only replace a very small fraction of transport fuel consumed in the US. However, as indicated in Fig. 2, the potential large-scale availability of lignocellulosic biomass could supply a high percentage of future liquid transport fuels, if commercial processes were available to convert these feeds. One such processing route evaluated in this study was applying commercially established fast pyrolysis of biomass to produce a pyoil intermediate and then converting it to transport fuels via thermochemical platforms.

An independent study by a national research laboratory suggests that there is a sustainable supply of about a billion tons of various biomass feedstock from agricultural and forest wastes annually in the US. Fig. 3 illustrates the results of this study. Feedstock availability is, therefore, not a constraint. But the challenge is developing the infrastructure to collect, to process and to convert these feed sources economically into biofuels.

Another study addressed both feedstock costs and projected prices of intermediate fuel products. Prices of raw vegetable oils, greases and pyrolysis oils were determined and used in this economic assessment. The costs ranged from $16/bbl for pyrolysis oil to >$75/bbl for raw vegetable oils. Each economic analysis was primarily based on a West Texas Intermediate (WTI) crude feedstock price of $40/bbl—a level considerably lower than 2007 WTI prices. The cost of each potential biofuel was compared to this crude feedstock price after incorporating a number of factors including capital costs, transportation costs, carbon dioxide (CO₂) credits, subsidies, and cetane and octane numbers. Most of the feedstocks looked promising when current subsidies were applied and several were economically attractive without subsidies such as pyrolysis oil and brown grease. Without subsidies, the break-even crude cost for raw vegetable oils is about $70/bbl.

The properties of biorenewable feedstocks were compared to petroleum, as shown in Table 2. The biggest difference between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels from 10% – 40% while petroleum has essentially none—making the chemical properties of biorenewables very different from petroleum. For example, biorenewable feedstocks are often more polar and some easily entrain water and can therefore be acidic. All have very low sulfur levels and many have low nitrogen levels depending on their amino acid content during processing. Several properties are incompatible with typical refinery operations such as the acidity and alkali content so that processes were identified to pretreat many of these feeds before refinery operations such as the acidity and alkali content so that processes were identified to pretreat many of these feeds before being tested over various thermochemical routes.

Refining opportunities for pyrolysis oil. Fast pyrolysis is a thermochemical process with the potential to convert the large volumes of cellulosic biomass available in the US and globally into liquid fuels and feeds. A solid biomass feedstock is injected into a fluidized 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, hemi-cellulose and lignin fractions present in the biomass. It also contains a high percentage of bio-oil.
of water, often as high as 30% as well as significant organic oxygen. The total oil is often homogeneous after quenching but can easily be separated into two fractions—a water soluble fraction and a heavier pyrolytic lignin fraction. Adding more water allows the pyrolytic lignin fraction to be isolated, and the majority of it consists of the same phenolic polymer as lignin but with smaller molecular weight fragments. The work reported here was done with whole pyrolysis oil.

Fig. 4 shows a scheme for hydro-processing pyrolysis oil to fuels. The pyrolysis oil is hydroprocessed in two steps. The first step substantially reduces the oxygen content and total acid number (TAN). The deoxygenated oil is then further hydroprocessed to produce a fuel. The research teams are also investigating the direct conversion scheme but there are significant technical and logistical hurdles associated with this approach.

Table 3 shows a performance for hydroprocessing pyrolysis oil to produce biofuels based on experimental results. These estimates were used as a basis for economic calculations. The naphtha and diesel range components are produced along with a large amount of water and CO₂ due to water removal and deoxygenation. Naphtha range and diesel range are based on the boiling point distribution of the hydroprocessed bio-oil hydrogen consumption, and the CO/CO₂ yield will vary depending on the mechanism of deoxygenation.

Table 4 shows the composition of multiple samples of the gasoline-range product from the two-step hydroprocessing and compares it to typical gasoline composition. The (RON+MON)/2 of this cut was about 90. The carbon recovery based on pyrolysis oil was about 50%.

The economics for producing naphtha range and diesel range fuels from pyrolysis oil are shown in Table 5, assuming $25/bbl pyrolysis oil cost and $70/bbl fuel value. This table shows that this process has the potential to exceed US Department of Energy targets for fuel cost based on an ethanol energy equivalent basis.

**Conceptual pyoil-based refinery.** A proposed pyoil based refining scheme is shown in Fig. 5. In this case, several distributed pyrolysis units would supply a central bio-refinery for conversion to fungible transportation fuels.

**Life-cycle analysis.** A life-cycle analysis was done to compare cradle-to-grave CO₂ emissions for pyrolysis-based gasoline and ethanol. The fossil CO₂ is substantially lower for pyrolysis oil to gasoline. Agricultural inputs are lower and less energy is needed for dehydration.

**Future.** Many economically attractive opportunities were identified in this study for the integration of biorenewable feedstocks and biofuels while applying thermochemical platforms. These bio-refineries can be designed to produce green gasoline and distillate fuels. Pyoil processing requires more development to enable large-scale commercially viable operations. In the long term, however, pyoil production can be ramped given the large amount of cellulosic biomass available, converted to transport fuels independent of the food chain and thus make a direct impact toward meeting a portion of the projected demand growth for fuels.

**ACKNOWLEDGEMENTS**

The authors acknowledge the US Department of Energy for having funded an earlier study (DOE Project DE-FG36-05GO15085) that formed the basis for further DOE-funded work by UOP, NREL, and PNNL.

**LITERATURE CITED**


4. Tyson, K. S., “Oil and Fat R&D,” Presentation by NREL to UOP.
Jennifer Holmgren is the director of UOP’s Renewable Energy and Chemicals business unit. She is responsible for the development and commercialization of new technologies and products for the processing of renewable energy sources. Dr. Holmgren received a BS degree in chemistry from Harvey Mudd College in Claremont, California, and a PhD in inorganic materials synthesis from the University of Illinois at Urbana-Champaign and an MBA from the University of Chicago. Previous assignments at UOP included the preparation and characterization of novel zeolites, molecular sieves and layered materials as well as a number of technology delivery projects in the BTX and olefins areas.

Rich Marinangeli is a principal scientist in the Renewable Energy and Chemicals Research Group. He has 30 years of experience at UOP in process development and catalysis and has 18 patents. Dr. Marinangeli holds a PhD in chemical engineering from Princeton University and a BS degree in chemical engineering from the University of Notre Dame. He was a CNRS Fellow in Villeurbanne, France prior to joining UOP.

Douglas Elliott is a staff scientist at the Pacific Northwest National Laboratory (PNNL). He has 34 years of experience at the laboratory since graduating with a BS degree in chemistry from Montana State University. He also holds an MBA in operations and systems analysis from the University of Washington. Mr. Elliott is the project manager at PNNL for biomass pyrolysis related projects. He holds 15 US and 42 foreign patents on technology related to biomass conversion to fuels and catalytic and thermal processing.

Dr. Richard Bain has been at the National Renewable Energy Laboratory (NREL) since February 1990, and has extensive experience in the thermal conversion of biomass, municipal wastes, coal and petroleum. He leads the Biorefinery Analysis Team in the NBC. He is a lead researcher in the area of production of transportation fuels via biomass thermochemical conversion. Dr. Bain is a technical advisor to the Department of Energy on biomass demonstration. He has been a member of the International Energy Agency Biomass Gasification Working Group for 17 years. Dr. Bain has published more than 70 papers and holds 10 patents in energy.

---

**Fig. 5** Distributed pyrolysis and centralized pyrolysis oil processing options.

**Fig. 6** Life-cycle analysis of pyrolysis-based gasoline.