

Transportation fuels from biomass via fast pyrolysis and hydroprocessing

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Biomass is a renewable source of carbon, which could provide a means to reduce the greenhouse gas impact from fossil fuels in the transportation sector. Recycling of carbon dioxide from the atmosphere, either by direct chemical conversion or via biomass growth based on solar energy provides the only renewable source of liquid fuels, which could displace petroleum-derived products. Fast pyrolysis is a method of direct thermochemical conversion (non-bioconversion) of biomass to a liquid product. Although the direct conversion product, called bio-oil, is liquid; it is not compatible with the fuel handling systems currently used for transportation. Upgrading the product via catalytic processing with hydrogen gas, hydroprocessing, is a means that has been demonstrated in the laboratory. By this processing the bio-oil can be deoxygenated to hydrocarbons, which can be useful replacements of the hydrocarbon distillates in petroleum. While the fast pyrolysis of biomass is presently commercial, the upgrading of the liquid product by hydroprocessing remains in development, although it is moving out of the laboratory into scaled-up process demonstration systems.

The reactivity of the oxygenates in bio-oil results in difficulties in further use and processing of the bio-oil. Bio-oil can be preheated to only a limited degree, up to about 40°C appears reasonable. Therefore, the catalytic processing required to remove the oxygen and produce a hydrocarbon fuel, which is typically done at 350-450°C, is done only with some special handling. The overall concept of biomass to liquid fuels via fast pyrolysis and hydroprocessing is shown in Figure 1.

Direct processing of bio-oil in conventional hydroprocessing systems has led to failure in several cases. Moderate pretreatment at lower temperatures (sometimes referred to as hydrotreating, HT) prior to the finishing hydroprocessing (sometimes referred to as hydrocracking, HC) has shown promise. The concept was first patented based on the early work in the 1980s.ⁱ Further developments and improvements have been more recently reported.ⁱⁱ Long-term trouble free operation has not yet been definitively reported, but there are claims in the non-technical literature.ⁱⁱⁱ

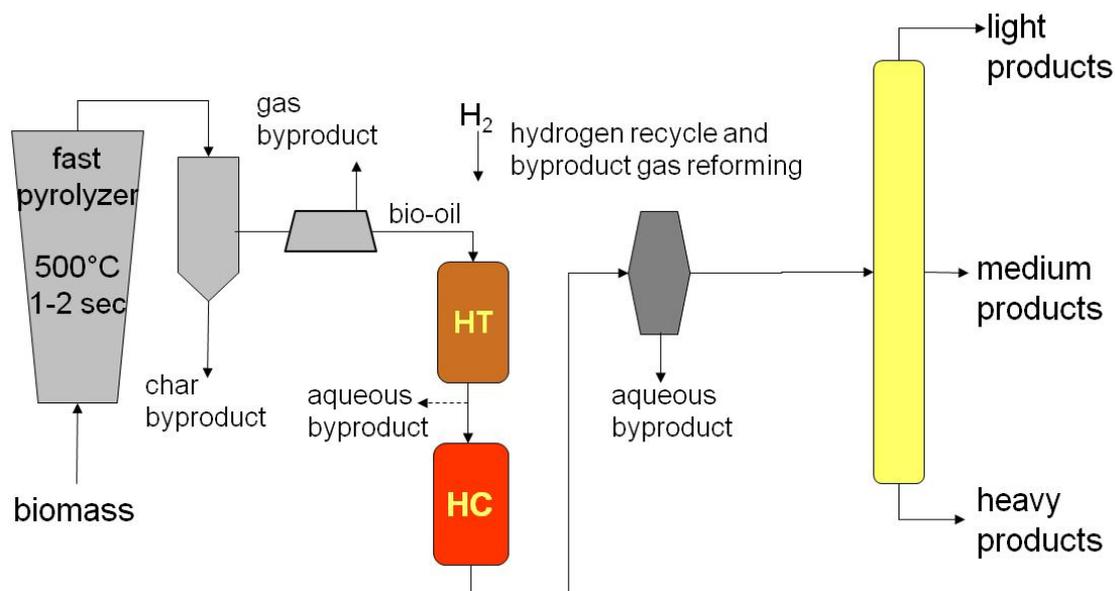


Figure 1. Hydrotreating of Fast Pyrolysis Bio-oils

BIO-OIL HYDROPROCESSING

Bio-oil can be deoxygenated by two theoretical routes: the oxygen can be thermally cracked from the bio-oil in the form of water and carbon oxides or it can be removed as water by addition of hydrogen. Both routes have been tested using different catalysts. Catalytic cracking has a capital cost advantage because of a lower cost reactor which operates at low pressure and higher throughput. Catalytic hydroprocessing uses more expensive equipment due to the higher pressure and slower throughput and also has a hydrogen reagent cost; however, it typically has a higher yield overall. The current process development efforts focus for the most part on hydroprocessing. Some of the work has used model compounds and been directed at more fundamental chemistry questions.^{iv} Other studies have investigated traditional sulfided catalysts while some have investigated non-sulfided precious metal catalysts reactors.^v Studies have determined that much, but not all, of the hydrogen requirement can be derived within the process from reformed gas byproducts.

Reactor Configurations

Conventional hydroprocessing of petroleum to finished fuels is performed almost exclusively with fixed catalyst bed operation. Similarly, most of the bio-oil processing has also been performed in fixed bed reactors. The scale of such operations has been limited to bench-scale reactors. Scale-up of the process is underway and should be on line in 2014 or 2015.^{vi}

The operation of the bio-oil catalytic hydrotreating process has similar concerns as that found with petroleum hydroprocessing. The oil feedstock needs to be relatively free of unreactive solids and preferably will be low in metals content. Distribution of the oil over the whole bed is a concern in order to maintain the highest efficiency of contacting the catalyst. The flow rate over the catalyst bed needs to be carefully controlled in relation to the process kinetics. The reported rates of

hydrodeoxygenation of bio-oil are relatively low, typically about 0.15 volume of bio-oil per volume of catalyst bed per hour, in order to approach complete deoxygenation. The exothermic nature of these hydrodeoxygenation reactions, which form water, is severe. Temperature increases as much as 60°C have been reported in small fixed beds^x and are expected to be a significant design factor in scale-up of the system.

The catalysts used have included both conventional promoted molybdenum sulfides (CoMo and NiMo) and also precious metal catalysts. When using sulfided catalysts an important concern is maintaining the sulfided nature of the catalyst when the bio-oil may actually be deficient in sulfur. Alternatively, when using precious metal catalysts, the amount of sulfur in bio-oils, even from clean wood at 50 ppm or less, may still be sufficient to deactivate the catalyst in the long term.

The primary issue interfering with long-term operation has been the fouling of the catalyst bed by carbonaceous deposits. These deposits appear to be condensation reaction products forming at elevated temperature from the most reactive components in the bio-oil. Low temperature hydroprocessing of the bio-oil prior to conventional hydroprocessing appears to ameliorate this problem. Refinement of the processing conditions to allow long term operation remains at the forefront of the process R&D.

Product Properties

Dependent on the processing severity, a range of deoxygenated products can be produced from bio-oil catalytic hydroprocessing. Nearly deoxygenated hydrocarbons (<0.5 wt% oxygen) have been of most interest. These product mixtures are different from petroleum crudes in that they are high in cyclic hydrocarbon structures, both saturated (naphthenes) and aromatic. These cyclic structures are clearly derived from the cyclic structures in the bio-oil itself. With less severe processing, higher space velocity or lower temperature, more oxygen is left in the product mix. The most stable oxygenates, and the last to be eliminated, have been reported to be the phenolics.^{vii}

Chemical Composition

The use of ¹³C nuclear magnetic resonance spectrometry has been found useful for identifying the functional groups residing in the process bio-oils. Although this method does not specify the actual chemical compounds in the product, it is helpful to distinguish the relative amounts of functional types of carbon in the hydroprocessed bio-oil. Through quantitative methods, carbon can be categorized into saturated and unsaturated carbon, as well as different oxygen-containing functional types, like carbonyls, phenolics, ethers, carboxylic acids, etc.

As for specific chemical components, alkylated benzenes and alkylated cyclohexanes are most commonly found by gas chromatography-mass spectrometry (GC-MS). Bicyclics, both saturated and aromatic, are also found by GC-MS. Through the use of other types of liquid and gas chromatography, other oxygen containing components can be identified in the products.

Physical properties

Since oxygen plays a big role in the physical properties of the chemical components in the hydroprocessed bio-oil, physical properties such as density viscosity and color can be correlated to the oxygen content in the oil. Density measurement is a simple way to determine the state of the

catalytic processing. Effective hydrodeoxygenation to remove oxygen to levels of less than 10% will reduce the density of the product to less than 1 g/ml from 1.2 g/ml for the starting bio-oil; and the trend continues downward with density nearing 0.9 g/ml with 5% oxygen remaining, and closing toward 0.82 g/ml as the oxygen is further reduced to levels approaching 0.^{viii}

Only limited fuel testing has been done on these hydroprocessed bio-oil products due to lack of product because of the small scale operations, so far. For example, research products from tests performed over a two year period were collected and segregated to recover sufficient material to distil a gallon of jet fuel range product.^{ix} In another case, a liter each of an 8.2%, 4.9% and 0.4% oxygen-containing hydroprocessed bio-oils were produced from products collected over 4 years. The amount of these products was just sufficient to process through typically crude petroleum analytical methods first to fractionate them into representative fractions, and then perform typical fuel analyses.^{xx}

Use as petroleum refinery feedstock

One goal of the analyses mentioned above was to determine the appropriate level of hydroprocessing required to produce products of sufficient quality to be processed within the existing petroleum refining infrastructure. A liter each of an 8.2%, 4.9% and 0.4% oxygen-containing hydroprocessed bio-oil was produced by collection and combining of products collected from many bench-scale hydrotreating tests. These products were processed through typical petroleum analytical methods first to fractionate them into representative fractions of light naphtha, gasoline, diesel, light cycle oil, heavy cycle oil and resid, and then perform typical fuel analyses. The study concluded that the 0.4% oxygen product had several options for refinery processing and should be acceptable feedstock. The 4.9% product had some interesting possibilities that would need to be analyzed and developed. The 8.2% product was not considered a reasonable feedstock for existing petroleum refinery operations.^x

The rationale for these analyses is the potential to produce bio-oil in small scale in a distributed fashion in proximity to the biomass resource, thereby reducing the transportation costs for raw biomass. The transporting of bio-oil to a central upgrading facility allows the scale-up efficiencies to be attained. In addition, if the upgrading facility is close to a petroleum refinery, which would be operating at even a larger scale, there is potential for additional savings for byproduct gas utilization for hydrogen production and other infrastructure interactions.^{xi}

Direct fuel blending possibilities

Hydrotreated bio-oil products from bench-scale tests were collected and segregated to recover sufficient material of appropriate quality (less than 0.5% residual oxygen) to distil a jet fuel range product. This distillate was further treated to reduce the oxygen content from 0.2% following hydroprocessing to 0.02 percent before blending. The upgraded fast pyrolysis product was blended with synthetic paraffinic kerosene from vegetable oil to produce the first entirely biomass-based turbine fuel. The cyclic and aromatic nature of the pyrolysis product provided the appropriate jet fuel properties in combination with the straight chain aliphatics from the lipids, and the fuel blend met the requirements for the engine manufacturer. The demonstration of the fuel was the operation of an unlimited class hydroplane for a single test of 3 laps around a 2.5 mile course.^{xxii}

The corrosion issue is also addressed by the deoxygenation of the bio-oil. Corrosion tests of hydroprocessed bio-oil, as a pure component, confirm that the reduction to <0.5% residual oxygen reduces the corrosion properties to a very low level. Based on 500 h exposure at 50°C, the rate on carbon steel as well as the several stainless steels tested was negligible.^{xii}

CONCLUSIONS

The use of fast pyrolysis to produce liquid products from solid biomass has been demonstrated commercially. Catalytic hydroprocessing can be applied to the bio-oil product from fast pyrolysis to deoxygenate the bio-oil and produce hydrocarbon products that can serve as renewable transportation fuels. The process development of the hydroprocessing is just moving to scale up from the laboratory. Larger quantities of product should be available in the near future to allow extensive testing and validation of the fuel properties.

ⁱ Elliott, DC; Baker, EG "Process For Upgrading Biomass Pyrolyzates." U.S. Patent Number 4,795,841, issued January 3, 1989.

ⁱⁱ Elliott, DC; Hart, TR; Neuenschwander, GG; et al. "Catalytic Hydroprocessing of Biomass Fast Pyrolysis Bio-oil to Produce Hydrocarbon Products." *Environmental Progress & Sustainable Energy* 28 (2009) 441-449.

ⁱⁱⁱ Dynamotive webpage

^{iv} Honkela, ML; Viljava, T-R; Gutierrez, A; Krause, AOI "Hydrotreating for Bio-Oil Upgrading" in *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*, RSC Energy and Environment Series No. 1, Royal Society of Chemistry, 2010, Cambridge, UK, pp 288-306.

^v Elliott, DC "Historical Developments in Hydroprocessing Bio-oils." *Energy & Fuels* 21 (2007) 1792-1815.

^{vi} Biello, D "First Dedicated Biorefinery Could Wean Hawaii Off Imported Oil" *Scientific American* April 10, 2012. <http://www.scientificamerican.com/article.cfm?id=first-biorefinery-could-wean-hawaii-military-off-imported-oil>

^{vii} Christensen, ED; Chupka, GM; Luecke, J; et al. "Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions" *Energy & Fuels* 25 (2011) 5462-5471.

^{viii} Elliott, DC; Hart, TR; Neuenschwander, GG; Rotness, LJ; Olarte, MV; Zacher, AH; Solantausta, Y "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust." *Energy & Fuel* 26 (2012) 3891-3896.

^{ix} Bertelli, C "Current Status of Biofuels Production and Use for Commercial Aviation" *BIO 2010 -V Seminario Latinoamericano y del Caribe de Biocombustibles*, Santiago, Chile August 17-18, 2010. http://www.olade.org/biocombustibles/Documents/Ponencias%20Chile/Sesion%204_C%20Bertelli_UOP_USA.pdf

^x Arbogast S, Bellman D, Paynter JD, Wykowski J. Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities. *Fuel Processing Technology*, doi: 10.1016/j.fuproc.2012.04.036.

^{xi} Holmgren, J; Marinangeli, R; Nair, P; et al. "Consider Upgrading Pyrolysis Oils into Renewable Fuels." *Hydrocarbon Processing*, 87 (2008), 95-103.

^{xii} Keiser et al "Corrosivity and Composition of Raw and Treated Pyrolysis Oils." *TAPPI*, October 2012.