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Hydrothermal Processing of Biowastes

R. Divyabharathi* and P. Subramanian
Department of Renewable Energy Engineering, AEC&RI,
Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu

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Introduction:

India has a significant need for liquid fuels and is the fourth-largest consumer and net importer of crude oil and petroleum products in the world after the United States, China and Japan. India's petroleum product demand reached nearly 3.7 million barrels per day (bbl/d), far above the country's roughly 1 million bbl/d of total liquids production. Efforts are needed to find alternate ways to replace fossil fuels with more environmentally friendly alternatives as potential solutions to the current energy crisis and associated environmental problems of India. More than 70% of India's population depends on biomass and about 32% of the total primary energy use in the country, mainly in rural areas is still derived from biomass. The current availability of biomass in India is estimated at about 500 million metric tonnes per year with estimated surplus biomass availability at about 120–150 million metric tonnes per annum, which shows a potential of about 18,000 MW (MNRE, 2021).

The generally adapted thermo chemical biomass conversion technologies are combustion, gasification and pyrolysis. Unlike these thermo chemical conversion processes dry biomass, hydrothermal liquefaction (HTL) converts wet waste biomass to a liquid fuel called biocrude oil. In HTL, water serves as the reaction medium, this eliminates the need to dewater biomass which can be a major energy input for biofuel production. In this conversion process, elevated temperature (200–350ºC) and pressure (5–20 MPa) is used to break down and reform biomass macromolecules into biofuel (Vardon *et al.*, 2011), subsequently referred to as biocrude oil. The recovered biocrude oil can be directly combusted and used as marine fuel or upgraded by integrating downstream processes to approach petroleum oils.

What happens in hydrothermal liquefaction?

HTL has been evaluated as a conversion technology for a wide range of biomass feedstock, ranging from agricultural and forestry waste, sewage sludge, algae and animal wastes (Wang, 2011). These feedstocks are all comprised of a complex mixture of constituent materials, including proteins and amino acids, fats, cellulose, hemicellulose and lignin. HTL operates at a temperature range of 200 to 350ºC, pressures up to 20 MPa with residence time from 0.2 to 1 hour. Under these processing conditions, the general pathway of conversion that takes place is hydrolysis, decarboxylation and repolymerization of some of the smaller compounds into more complex hydrocarbons. It is important to note that only the volatile, or organic components of the biomass can be converted to biocrude oil via HTL. Research has indicated that feedstock that is higher in protein and lipid concentration leads to a higher oil product yield, while those higher in fibrous material lead to higher biochar yields.

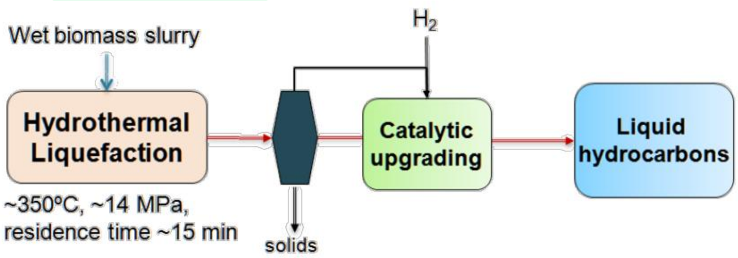

Figure1: Overview of HTL process

Products of HTL:

HTL processing of manure yields four product streams: biocrude oil, synthesis gas (syngas), biochar and wastewater effluent (aqueous phase). The feedstock and processing conditions will impact the exact makeup and distribution of these product streams. It should be noted that for most HTL processes, the water content in the initial feedstock is the major component, providing at least 75% of the total mass of the feedstock, and therefore a majority of the product output is water effluent. The volatile solids content of the manure is the convertible fraction of the feedstock.

Biocrude oil: The biocrude oil produced from the liquefaction of wet wastes is a complex mixture of hydrocarbons. The bio-oils produced from liquefaction typically have a lower oxygen content and a higher heating value than those produced by pyrolysis (Huber *et al.*, 2006). Biocrude oil yields have ranged from 20 %wt. to 70 %wt. with respect to volatility, depending on feedstock and processing conditions. The biocrude oil is mostly made up of carbon, hydrogen and oxygen, with lesser amounts of nitrogen, sulfur, ash and water.

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Liquefaction bio-oils have been evaluated for a variety of end uses, most commonly used as a replacement for petroleum fuels, for either heating or transportation applications. Higher concentrations of nitrogen and sulfur in biocrude oils produced from HTL have limited their direct use for fuel applications, however, they have shown heating values upward of 12,898 BTU/lb (Zhang *et al.*, 1999). Additional applications include use as a replacement for petroleum derived asphalt in road construction and roofing (Fini*et al.*, 2011). As with most bio-oils produced via thermochemical conversion, HTL biocrude oils are chemically unstable without further upgrading or modification to use as transportation fuel like petrol and diesel, however, they are stable than pyrolysis oil and can be directly used as furnace oil or as a marine fuel.

Syngas: The syngas produced in hydrothermal liquefaction is mostly comprised of carbon dioxide (He *et al.*, 2000). The use of CO as a reducing process gas will also increase the amount of CO_2 produced as syngas. For most studies of HTL processing, the syngas was simply vented and not evaluated further. However, a more complete evaluation of the components within the gas stream would be required, to ensure that the production of other gases, such as methane, CO and H_2S, remain at low enough concentrations to be considered negligible

Biochar: The biochar, or solid residue, produced from HTL processing of manure is mostly composed of the inorganics (ash) from the small amounts of unreacted feedstock, and char formed during the reaction. Biochar produced from HTL processing may have applications as a soil amendment, filtration media, or filler in industrial applications.

Wastewater (Aqueous phase): The wastewater effluent produced from the HTL processing is mostly comprised of H_2O, which was originally in the feedstock and was generated during the process. In addition, the majority of non-condensable hydrocarbons, fixed carbon and nutrients, including N, P and K remain with the wastewater effluents. This chemical rich aqueous phase can be used to derive value added fuels and chemicals and in areas where nutrients can be applied to land, this aqueous phase may serve as a nutrient source. However, in some areas, this effluent may require additional treatment prior to land application or discharge.

Figure2: Products obtained from HTL

HTL recommendations and future scope:

HTL of wet biomass obtained biocrude oil yields more than 30 %wt. (>50% yield on a carbon basis). The biocrude oil contains 10% oxygen on a dry basis, which is significantly lower than the oxygen content in fast pyrolysis oil. The low oxygen content correlates to an improvement in the total acid number (TAN) of the oil as 30. The oil is thermally stable, which is a benefit for upgrading to final hydrocarbon fuels. The HTL oil needs to be hydrotreated to further remove the remaining oxygen and produce petroleum refinery intermediates to hydrocarbon fuels in the gasoline and diesel range. Challenges still exist. HTL requires reactors that can operate at high operating pressures, which adds capital cost; the oil that is produced is thick and viscous like corn syrup, and too much of the biomass is converted to something other than the oil. Further research is needed to solve these issues to lower the cost of biocrude oil production for fuels that can blend at high ratios within our current fuel supply.

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