HYDROTHERMAL LIQUEFACTION

www.merrick.com | hello@merrick.com

By Michael Washer

Liquid and moisture laden waste streams are a large, and growing, problem in the US, and globally. These waste streams include wastewater treatment solids, animal waste, fats, oils & greases (FOG), black liquor, and food waste. Regulations and limits on landfilling and land application of many of these wastes get tighter, so disposition pathways get more expensive.

This article shows that there is a solution to this problem. Hydrothermal liquefaction (HTL) enables wet waste streams to be converted to bio-oil, which can then be hydro-treated to produce a bio-crude that is compatible with existing oil refinery infrastructure.

Table 1 shows a summary of the annual wet waste availability, along with the inherent energy content, and the liquid fuel equivalent value of that energy, expressed as gasoline equivalent (Ref 1).

Table 1: Wet Waste Availability and Energy Content

Feedstock	Estimated Annual Quantity (MM Dry Tons)	Energy Content (Trillion Btu)	Liquid Fuel Equivalent (MM GGE)[1]
Wastewater Sludge	14.82	237.6	2046.6
Animal Waste	41.00	547.1	4713.0
Food Waste	15.3	318.2	2741.3
Fats, Oils & Grease	6.05	214.3	1845.8
Glycerol	0.6	8.7	75.1
Black Liquor	44	517.4	4456.5
Total	**121.77**	**1843.3**	**15878.3**

[1] GGE is gallons of gasoline equivalent.
1 gal gasoline = 116,090 Btu. This does not account for conversion efficiency.

Clearly the energy content and liquid fuel equivalent values are hypothetical, since 100% recovery of the liquid fuel value is not possible. However, the values illustrate the sheer quantities of wet waste that currently require disposal, and the potential product volume if a meaningful proportion of this material can be converted to liquid fuel.

Much focus has been directed at wet waste processing technologies that include concentration or drying of the material, to produce either a solid, or a high solids liquid stream. These can then be fed to a boiler or burner, as fuel, or to a gasifier. The common element to these approaches is that the moisture is driven off the fuel. With the exception of FOG and glycerol, these waste streams are relatively dilute, typically >80wt% moisture. Thus, driving off this moisture requires a lot of energy, typically more than the energy content of the fuel produced.

HTL represents a processing technology that precludes the need to evaporate or dry the waste feed prior to conversion to fuel. In fact HTL requires that the feed be aqueous. HTL enables the conversion of the organic components in the feed to bio-oil and bio-gas. Furthermore, it precipitates the inorganic components of the feed, enabling them to be recovered. These are often phosphorous, nitrogen and sulfur compounds, which are valuable as fertilizers.

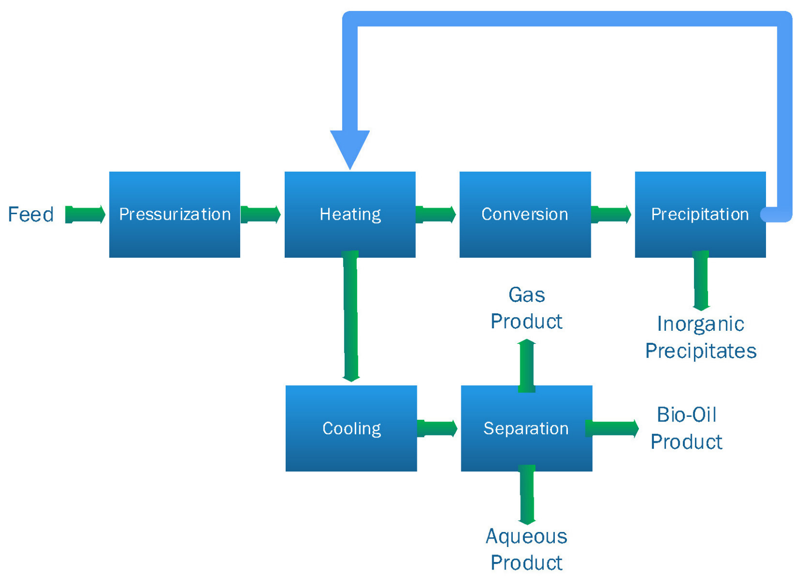
The concept of heating wet biomass to produce oil has been around since the 1920's. The technology was first explored in detail in the 1970's, during the oil crisis. It was investigated by a range of public and private entities, including Shell Oil.

More recently the National Advanced Biofuels Consortium (NABC) was established in the U.S. to develop "drop-in" fuels derived from biomass feedstocks. This consortium performed research, testing, and analysis on a range of technologies, including HTL. The HTL team was led by the Pacific Northwest National Laboratory (PNNL).

As well as wet wastes, HTL processing of algae and other fast-growing plant species (e.g. duckweed, water hyacinth) has also been investigated. It has been shown that HTL can process practically any wet material that can be pumped into the system. Arguably, processing of wet wastes offers the highest commercial potential in the US and Western Europe, due to the negative cost of the feedstock, i.e. the HTL processor is paid to accept the waste, and convert it to a saleable product. This creates revenue streams from the feed and product of the process.

The exact equipment configuration of an HTL process varies by application, but the general processing scheme is shown in Figure 1 below.

Figure 1. HTL Process Blow Flow Diagram



HTL processes operate at elevated temperatures, typically 300-360°C. At these temperatures, in order to suppress boiling, the HTL processes are operated at 1400-2800psig. These conditions are below the critical point of water, although some research has been conducted into supercritical HTL processing. At the processing conditions, the organic materials in the feed break down to form bio-oil and some gases (principally methane and CO2). The residence time in the conversion step varies, depending on the nature of the feed, and the process conditions, but is in the range of 10-30 minutes. Testing to date has shown that the conversion step can be performed in a stirred tank reactor, or a plug flow reactor, with a minimal difference in performance between them. A curious property of water at the processing pressure and temperature is that the solvent properties are inverted from the solvent properties of water observed at lower pressure and temperature. Specifically, the bio-oil produced by the degradation of the organic components of the feed become water soluble, and the inorganic materials become almost insoluble. This has very useful implications for the process. It enables the inorganic fraction to be separated from the bulk of the water and oil in the precipitation step. Once the oil and water has been cooled, the bio-oil is no longer soluble in the water. The oil and water, along with the associated gas, can be separated in a 3-phase separator. Figure 2 shows the product from pilot plant testing of HTL, with algae feed.

Figure 2. Bio-Oil Product From HTL Processing Of Algae

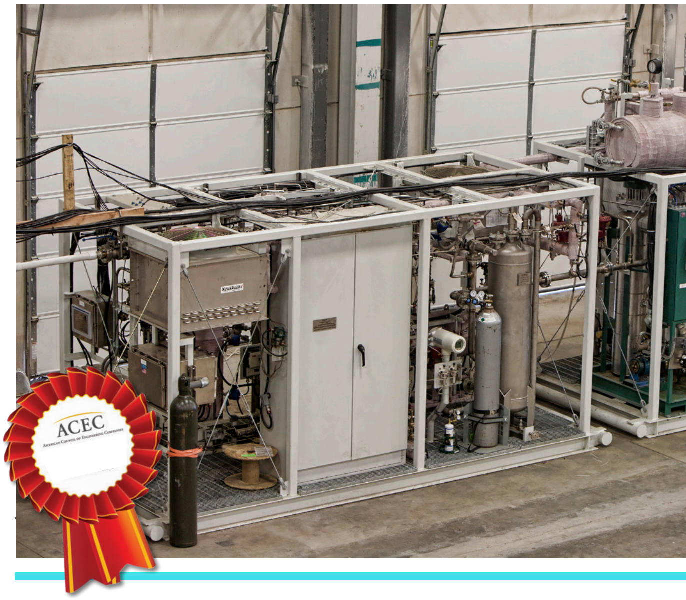
PNNL has been researching HTL for many years, and has built several pilot plants, to test a range of feedstocks, operating conditions, and equipment configurations. The results of the PNNL testing have been published in a number of reports. These include techno-economic analyses of HTL processing (Ref 2).

The principle and practice of converting wet, organic materials to bio-oil and gas has been proven at the lab, bench, and pilot scale. As such, the core process technology has been proven. As is typical with a new process, particularly in the bio-processing arena, there are a number of additional challenges to be overcome before HTL can be commercialized.

- Capital cost – In an era of prolonged low oil prices, revenue from the production of bio-oil will be depressed. Thus the economic viability of HTL depends on driving down the capital cost of commercial systems. Several strategies are being pursued for this
  - Standardization – development of standardized system designs, to minimize engineering costs for multiple units.
  - Modularization – to enable HTL systems to be built, assembled and tested in a factory environment, then shipped to the customer site ready to use.
  - Scale-up – Reducing the unit cost (i.e. cost per gallon of feed) of processing by increasing the system size.
  - Low cost components – The combination of high operating pressure and temperature make HTL an inherently costly endeavor, but there is a strong driver to identify equipment and instrumentation that can deliver the required performance at the lowest cost.
- Energy recovery – Heating the feedstock from ambient to the conversion temperature (300 360°C) is inherently energy intensive. The economics of HTL processing hinge on either
  - Finding a low-cost energy source, available at a high temperature, or
  - Using the thermal energy of the process stream to heat the feed stream. This is a topic of great interest, and is currently being explored. It should be possible to recover 80-90% of the heat from the product stream.
- Processing of the precipitated inorganic components to recover them in a useful form - It has been shown that the inorganic constituents of the feed can be precipitated and separated from the process stream. More work is required to develop a process that generates a product, likely a fertilizer, which can be commercialized.
- Post-treatment of the bio-oil to make it suitable for standard refining - The bio-oil produced by the process is typically very acidic and has a high oxygen and nitrogen content. This is not suitable for feeding to existing refinery processes, even by blending with conventional refinery process streams. PNNL has conducted testing which shows the bio-oil can be hydrotreated to lower the acidity and oxygen content, to the point they are comparable with crude oil. More work is needed to develop this post-processing of the bio-oil, to the point that an existing refiner will buy the product.
- Treatment of the wastewater – no process conversion step is 100% effective. The wastewater from the HTL process still contains organic compounds, which must be removed. A supplemental process, called Catalytic Hydrothermal Gasification (CHG) has been developed and tested at the bench and pilot scale. This passes the HTL product water over a catalyst, which converts the organic compounds to primarily methane. This can be separated from the liquid and either used directly as a fuel, or processed for injection into a natural gas pipeline. Alternatively, it may be possible to route the HTL wastewater to a wastewater treatment plant. If the HTL process is located at a wastewater treatment plant, the logistics of this are relatively straightforward.

The number of companies pursuing HTL demonstrates that the technology is increasingly garnering interest. Industry and public awareness of HTL was raised by the national ACEC Honor award for the Hydrothermal Processing Pilot System (HPPS) project.

In summary, Hydrothermal Liquefaction shows a lot of promise for converting wet wastes to liquid fuels. There is much work to be done before it can be commercialized, but there are a number of companies with their shoulders to the wheel, working to make this technology part of the energy landscape.



Hydrothermal Processing Pilot System
Merrick & Company, Greenwood Village, CO
Client: Genifuel Corporation

This pilot project proved that a hydrothermal processing system can be used to transform wet biomass waste into a valuable fuel at a useful scale. Hydrothermal processing uses water, high heat, and high pressure to transform hydrocarbon-rich material - in this test case, algae - into bio-crude oil and natural gas. While the technology has been successfully tested in laboratories, this project was the first time in a pilot-scale of the processing system was successfully built, tested, and commissioned. Currently now in operation in India, the pilot-scale system produces approximately 1,000 liters of fuel per day - a much higher quantity than any previous demonstration of the technology, and an indicator of its potential for other, larger applications.

References:

1. Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities - U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office, January 2017.

2. PNNL-25464, Hydrothermal Liquefaction and Upgrading of Municipal Wastewater Treatment Plant Sludge: A Preliminary Techno-Economic Analysis, LJ Snowden-Swan, RT Hallen, Y Zhu, JM Billing, SB Jones, TR Hart, DC Elliott, SP Fox, AJ Schmidt, GD Maupin, June 2016.