Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review

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Athanasios Dimitriadis, Stella Bezergianni*

Laboratory of Environmental Fuels and Hydrocarbons – LEFH, Centre for Research and Technology Hellas – CERTH, 6km Charilaou-Thermi, Thessaloniki, Greece

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ABSTRACT

The continuing use of fossil fuels accelerated the energy crisis, environmental pollution, and global warming in recent years. These problems are the driving force of the worldwide search for new alternative energy, among which biomass is considered to be one of the most promising candidates due to its renewable, carbon neutral and high productivity characteristics. Hydrothermal liquefaction (HTL) is an alternative technology of exploiting different types of biomass for fuels production, involving the direct biomass conversion to liquid, in the presence of a solvent and in some times catalyst. HTL has undergone a sudden increase in the number of publications in recent years. The wide variation in different types of feedstock tested, their initial state, the reaction conditions and/or the catalysts applied renders a wide but rather fragmentary spectrum of knowledge generated. This review is a summary of state-of-the-art knowledge of HTL for various feedstocks such as woody biomass, wastes, plastics and microalgae.

1. Introduction

The rapid global energy demand increase imposes the need for new energy sources and raises the interest in renewable energy production technologies. Thermo-Chemical Conversion (TCC) technologies are not new fuel production pathways, as they have been widely studied since 1788 for biomass conversion to biocrude products [1,2]. Nevertheless, the biomass TCC technologies have been abandoned due to the low petroleum prices, and only until recently have they been revisited in an attempt to meet the growing energy demands worldwide as well as the environmental concerns regarding conventional fossil energy production and utilization.

The main biomass TCC technologies are gasification, hydrothermal liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction. Gasification converts biomass into synthesis gas (mainly hydrogen, carbon monoxide, carbon dioxide and methane) [3,4]. Even though it is considered a flexible process regarding the types of biomass it can convert, it renders a gaseous product that needs to be converted to fuel via an auxiliary process such as Fischer-Tropsch synthesis. Direct combustion of biomass is widely applied but only for electricity production [5]. Supercritical Fluid Extraction (SFE) is a process for separating two components by using supercritical fluids as the extracting solvent. Applications of SFE include separations of biological fluids, bioseparation, petroleum recovery, crude de-asphalting and dewaxing,

coal processing, selective extraction of fragrances, oils and impurities from agricultural and food products and many other applications [6]. However the use of high pressures leads to high operational and capital costs for SFE plants.

Biomass pyrolysis and hydrothermal liquefaction (HTL) are two comparable technologies, as they both render bio-based intermediate products (often referred to as oils or biocrude). However, the complex associated reaction pathways of these technologies are not yet clear, and many researchers are at present focusing in understanding them. There are, however, significant differences between these two technologies (Table 1). Feedstock drying is required for the pyrolysis process, while it is not necessary in the case of liquefaction which reduces the economic return of fuel production to a great extent due to the wet nature of the selected feeds [7]. Furthermore, the use of catalyst enabling the reactions is not common in pyrolysis, while the solvents employed for HTL act as catalysts, rendering higher quality products as compared to those obtained from pyrolysis. Finally, the HTL product has lower oxygen and moisture content and higher heating value in comparison to the pyrolysis product which reduces both the fixed and operative costs of handling equipment and storage [8], rendering the HTL technology more competitive for biomass conversion to fuel products [9], as indicated in Table 1. Nevertheless, it should be noted that the high pressure operation raises the investment costs of HTL units.

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* Corresponding author.
  E-mail addresses: adimitr@cperi.certh.gr (A. Dimitriadis), sbezerg@cperi.certh.gr (S. Bezergianni).

Table 1

Comparison of Hydrothermal Liquefaction and Pyrolysis processes for biomass conversion [10–14].

	Pyrolysis	Liquefaction
Drying	Necessary	Unnecessary
Pressure (MPa)	0.1–0.5	5–20
Temp (°C)	370–526	200–400
Catalyst	No	Some times
Heating Value	Low (~17 MJ/Kg)	High (~30 MJ/Kg)
Oxygen content	High	Low
Water Content	High	Low
Viscosity	Low	High
Upgrade	Hard	Easy

HTL, also known as hydrous pyrolysis [15], is a very flexible technology as far as the type of feedstock is concerned, as a wide variety of bio-based and waste feedstocks have been tested including woody biomass, industrial wastes, food wastes, swine manure, algae, arborous crops, wastes from forest industry etc. During the HTL process, biomass is directly converted to biocrude in the presence of a solvent and in some cases catalysts at temperatures lower than 400 °C. Most studies in the literature have been conducted in small scale batch type-reactors with slow heating rates and long residence times. In order for this technology to become more economically feasible and chemically controllable research in continuous reactors is required [16–18].

HTL takes place in high pressure and temperature with the presence of a solvent in order to form a highly reactive environment. The reactions that take place during HTL are decomposition and repolymerization forming biocrude, aqueous dissolved chemicals, solid residue and gas. High pressure helps solvent, which in most cases is water, to remain in the liquid state, while the combination of high pressure and temperature results in decreasing its dielectric constant and density, forcing hydrocarbons to become more water-soluble [17]. In addition to that, the polarity of water molecules decreases, as a result of a more evenly shared electron between the oxygen and hydrogen atoms. The increasing dissociation of water into H+ and OH− ions, suggests that the hot-compressed water is a good medium for acid- or base-catalyzed reactions [19].

HTL has undergone in recent years a sudden increase in the number of publications as a promising technology for biomass conversion. However, the knowledge generated is rather fragmentary, and for this reason this review aims to collect, analyze and evaluate the available experimental data. Comparing the research findings appeared to be quite challenging due to the wide variation in the different feedstock types, initial states, reaction conditions and/or catalysts utilized. This review summarizes the HTL state-of-the-art for the conversion of various bio-based and waste feedstocks such as woody biomass, wastes and algae.

2. The HTL process and yields calculations

Most of the research on HTL has been carried out in small (10–1000 ml) batch-type autoclave stirred reactors, made of stainless steel (SS316), allowing slow heating rates and long residence times (up to 1 h). The experiments are usually conducted under high pressure and medium heat provided by molten tin bath [20], small GC-oven [21], heating jacket [22] or external electric heaters [23]. The mixture of biomass, solvent and catalyst is introduced inside the reactor. An inert gas such as nitrogen or hydrogen is introduced to purge the residual air in the autoclave for some minutes; this step could be repeated from one to three times. Afterwards, the reactor is pressurized to the desired pressure with nitrogen or hydrogen without heating, and then it is heated to a specific temperature, allowing the reactions to start. It should be noted that with the rise in temperature, the pressure is

expected to gradually increase. The stirring is kept constant during the whole heating period up to the reaction temperature. Once the targeted temperature is attained inside the reactor, it is maintained for a specific holding time depending from the experiment conditions. After the holding time is passed, the stirring is off and the autoclave is cooled to room temperature either via an electric air fan, or via an ice bath, or by removing the heating jacket, or by using an internal cooling coil system. In most of the studies, once the reactor is cooled to room temperature, the gaseous product is vented, however, there are some studies were the gaseous product inside the reactor is collected into a gas-collecting vessel [24] or in a gas-sampling bag and the total volume is measured and analyzed [25]. Finally the reactor is depressurized and the autoclave is opened, allowing the careful removal of the products for further separation and analysis.

Besides the execution of the HTL batch experiments, equally important is the way that the desired biocrude is separated from the rest of HTL products, involving several methods of biocrude separation, the most common of which [13,23,26–28] will be described below. At the end of the experiment there are three types of products: gaseous, liquid and solid products. The gaseous product, which consists mainly of hydrogen and/or nitrogen, carbon monoxide, methane and carbon dioxide [29], is easily collected via a gas product system during the reactor depressurization; however, the solid/liquid mixture inside the reactor requires a certain separation procedure. After each experiment, the resulting mixture is filtered with paper to obtain a filtrate consisting of water and water-soluble organics and inorganics depending on biomass feedstock, HTL solvent and catalyst type, as well as the leftover solids. Then the reactor vessel is washed with a solvent such as acetone to recover the residual deposits from the reactor walls. The acetone solution is then collected, mixed with the mixture obtained from the previous step after filtration, and in most cases shaked well. The shaked mixture is filtered once again to obtain the organic phase and excess acetone, while the later is obtained via evaporation. The extracted liquid product is a dark brown viscous material (referred as the biocrude).

Once the biocrude is obtained, it is important to evaluate the HTL yield characterizing each experiment. HTL yields depend on different physical and operating parameters such as the lignin content of the feedstock, the solvents and catalyst, residence time, temperature and ratio of the solvent to biomass [9]. Significant variations (see Tables 3–6) were found in the way various researchers calculate the yields on their experiments and analyze the results, which makes it difficult to compare the data. The most commonly used yield calculations are summarized below.

Ye et al. [30], takes into consideration all the liquefied products, i.e. the aqueous fraction (AQ), the acetone-soluble fraction (AS), and the residue (RS). The overall HTL yield, as well as the percentage of the AQ and AS liquid products, are calculated via the following equations respectively:

$$\text{HTL yield}(\%) = 100 - (\text{residue mass/feedstock mass}) \times 100 \qquad (1)$$

$$\text{AQ percentage}(\%) = -(\text{AQ mass}/(\text{AQ mass} + \text{AS mass})) \times 100 \qquad (2)$$

$$\text{As percentage}(\%) = 100 - (\text{AQ mass}/(\text{AQ mass} + \text{As mass})) \times 100 \qquad (3)$$

According to Minowa et al. [26], the HTL yield is only defined by the desired liquid product yield, according to the following equation:

HTL Yield (wt%)=(organic mass in each product) /(organic mass in feedstock)×100.

Zhang et al. [14] considers the yield percentage of each HTL product, i.e. gas, liquid (biocrude) and solid residue product, defined as:

Gas yield(%) = (gas mass/feedstock mass) × 100.

Liquid yield (%)=(1−gas mass/feedstock mass−residue mass/feedstock mass)×100.

Residue yield(%) = (residue mass/feedstock mass) × 100.