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Review

# Fast hydrothermal liquefaction for production of chemicals and biofuels from wet biomass – The need to develop a plug-flow reactor

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#### HIGHLIGHTS

- No clear winner in HTL of biomass can be identified so far.
- Process intensification can help HTL to win.
- Fast heating combined with short residence time helps increase biocrude yield of HTL.
- Static mixing of pre-heated water with biomass solution offer high heating rates.
- Key issue for HTL of biomass is to develop a plug-flow reactor.

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#### ABSTRACT

Hydrothermal liquefaction (HTL) is a promising technology for converting wet plant biomass directly to liquid fuels and chemicals. However, some aspects of the technology are not fully understood and still disputed. The reactor material constraints and difficulties coupled with the formation of unwanted products are the main challenges limiting the applications of the technology. In addition, heat and mass transfer limitations in the reaction system result in a lower conversion efficiency and selectivity, of which the later would make it difficult and expensive for products separation, purification, and/or modification of the products. This paper discusses the challenges and current status of possible solutions to the challenges, focusing on the need of developing a special plug-flow reactor for scaling up of the HTL process. © 2016 Elsevier Ltd. All rights reserved.

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#### 1. Introduction

Replacement of fossil fuels by renewable energy alternatives (wind, solar, geothermal, hydropower, and biomass) has been becoming more and more important to cope with the global problems of climate changing, increasing energy demand, energy secu-

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http://dx.doi.org/10.1016/j.biortech.2016.04.002 0960-8524/© 2016 Elsevier Ltd. All rights reserved. rity and limitations of fossil fuel resources. Biomass is the only renewable energy resource that can replace fossil recourses in production of chemicals and liquid motor fuels. First generation biofuels, liquid fuels derived from food biomass, in full development, however, have been revealing severe shortcomings on increasing food price, limited CO<sub>2</sub> savings, and land degradation. Mankind are therefore turning to the use of plant lignocellulosic biomass and agricultural wastes, the most abundant global source of

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renewable organic matter, as feedstock to produce liquid fuels, which are referred as second generation bio-fuels.

A critical question concerning the use of plant biomass as an energy alternative (bioenergy) for a long-term perspective is whether the world's agricultural society will be able to cultivate plants for adequate substitution of fossil energy. While there are many uncertainties to answer this question, it is certain that aquatic biomass is more efficient at converting sunlight to chemical energy than most other biomass species. Microalgae and macroalgae have great potential as feedstock for biofuels production because of their rapid growth rates, high areal productivity, ability to sequester waste carbon dioxide (CO<sub>2</sub>), and strong potential for mass cultivation on marginal lands that do not compete with agriculture. Moreover, the use of nutrient-rich wastewater as a nutrient source for algal cultivation could increase the environmental sustainability of this process and reduce wastewater discharge of nitrogen and phosphorus. However, these wet biomass resources have normally very high water contents (89-90 wt.%). Anaerobic digestion (AD) is a common practice for biogas production from such wet biomass resources. However, the handling of digestate (residue) from AD biogas production is a problem, since the amount produced is too large to be used as fertilizer. Once burned, alternatively, the high water content of digestate reduces significantly the energetic efficiency of the process.

In the effort of obviating the capital, energy, and time required to dry such wet feedstock, many have developed hydrothermal processes for production of chemicals and biofuels. It is due to the fact that hydrothermal processing (HTP) employs hot compressed water (100–700 °C for temperature, and pressure up to 40 MPa) as reaction medium and therefore does not require drying the feedstock (Peterson et al., 2008; Brand et al., 2014; Elliott et al., 2015). Various applications (Fig. 1) of hydrothermal processing for production of chemicals and biofuels are possible, of which the majors are hydrothermal carbonization (HTC: 150–300 °C) producing solid fuels known as hydrochar (Heilmann et al., 2010; Libra et al., 2011; Chen et al., 2012), hydrothermal liquefaction (HTL: 300–374 °C) producing a liquid fuel known as biocrude or biooil (Singh et al., 2015; Zhou et al., 2010; Anastasakis and Ross 2011; Vardon et al., 2011; Elliott et al., 2013; Liu et al., 2013; Pham et al., 2013; Toor et al., 2013; Zhu et al., 2013; Bach et al., 2014; Fortier et al., 2014; Li et al., 2014; Neveux et al., 2014; Tian et al., 2014; Valdez et al., 2014; Venteris et al., 2014), and supercritical water gasification (SWG: higher than 374 °C) producing fuel gases (Schumacher et al., 2011; Onwudili et al., 2013; Bagnoud-Velásquez et al., 2014), as the main product. Other applications of HTP include hydrothermal hydrolysis (lower than 180 °C) (Redwood et al., 2012; Tsubaki et al., 2012; Xiao et al., 2013; Chimentão et al., 2014; Kim et al., 2014), and wet torrefaction (180-250 °C) (Chen et al., 2012; Bach et al., 2013, 2014; Reza et al., 2013), of which the latter is sometimes confused with HTC since there is no clear cut difference in definition between the two concepts with respect to operation temperature. However, wet torrefaction aims to produce advanced solid fuels for energy use only, whereas HTC produces hydrochar suitable for use as fuel, activated carbon, fertilizer and soil conditioner (Bach et al., 2013, 2014).

Among the aforementioned applications of HTP, HTL may become important technologies for converting wet biomass to biofuels and valuable chemicals, due to the possibility to develop continuous processes for commercialization (Matsumura et al., 2005; Knorr et al., 2013; Elliott et al., 2015). Indeed, early continuous flow processes of HTL have been developed since the 1970-1980 s (Elliott et al., 2015), including a laboratory work at Lawrence Berkeley Laboratory (Schaleger et al., 1982) and the Albany Biomass Liquefaction Experimental Facility (Thigpen, 1982), both in the US, and the Hydrothermal Upgrading (HTU) plant (Goudriaan et al., 2001) in the Netherlands. However, only small scales of HTL have been demonstrated for short time periods (Elliott et al., 2015). The largest demonstration of a version of the technology was the operation of the Albany Facility producing 52 barrels of product over the life of the facility (Elliott et al., 2015). No clear winner in this area can be identified so far. There was a

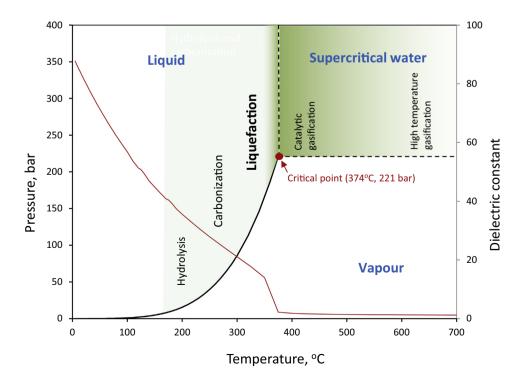


Fig. 1. Pressure-temperature (Moran et al., 2011) phase diagram of water and static dielectric constant (Archer and Wang, 1990) of water at 200 bars as a function of temperature.

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