Fast hydrothermal liquefaction for production of chemicals and biofuels from wet biomass - The need 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.

Keywords: *Hydrothermal liquefaction; HTL; Biomass liquefaction; Direct liquefaction.*

1. Introduction

Replacement of fossil fuels by renewable energy alternatives (wind, solar, geothermal, hydropower,

25 and biomass) has been becoming more and more important to cope with the global problems of climate
26 changing, increasing energy demand, energy security and limitations of fossil fuel resources. Biomass
27 is the only renewable energy resource that can replace fossil resources in production of chemicals and
28 liquid motor fuels. First generation bio-fuels, liquid fuels derived from food biomass, in full
29 development, however, have been revealing severe shortcomings on increasing food price, limited CO₂
30 savings, and land degradation. Mankind are therefore turning to the use of plant lignocellulosic biomass
31 and agricultural wastes, the most abundant global source of renewable organic matter, as feedstock to
32 produce liquid fuels, which are referred as second generation bio-fuels.

33 A critical question concerning the use of plant biomass as an energy alternative (bioenergy) for a
34 long-term perspective is whether the world's agricultural society will be able to cultivate plants for
35 adequate substitution of fossil energy. While there are many uncertainties to answer this question, it is
36 certain that aquatic biomass is more efficient at converting sunlight to chemical energy than most other
37 biomass species. Microalgae and macroalgae have great potential as feedstock for biofuels production
38 because of their rapid growth rates, high areal productivity, ability to sequester waste carbon dioxide
39 (CO₂), and strong potential for mass cultivation on marginal lands that do not compete with
40 agriculture. Moreover, the use of nutrient-rich wastewater as a nutrient source for algal cultivation
41 could increase the environmental sustainability of this process and reduce wastewater discharge of
42 nitrogen and phosphorus. However, these wet biomass resources have normally very high water
43 contents (89-90% wt). Anaerobic digestion (AD) is a common practice for biogas production from such
44 wet biomass resources. However, the handling of digestate (residue) from AD biogas production is a
45 problem, since the amount produced is too large to be used as fertilizer. Once burned, alternatively, the
46 high water content of digestate reduces significantly the energetic efficiency of the process.

47 In the effort of obviating the capital, energy, and time required to dry such wet feedstock, many
48 have developed hydrothermal processes for production of chemicals and biofuels. It is due to the fact
49 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, Vogel et al. 2008; Brand, Hardi et al. 2014; Elliott, Biller 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, Davis et al. 2010; Libra, Ro et al. 2011; Chen, Ye et al. 2012), hydrothermal liquefaction (HTL: 300-374°C) producing a liquid fuel known as biocrude or biooil (Singh, Bhaskar et al. ; Zhou, Zhang et al. 2010; Anastasakis and Ross 2011; Vardon, Sharma et al. 2011; Elliott, Hart et al. 2013; Liu, Saydah et al. 2013; Pham, Schideman et al. 2013; Toor, Reddy et al. 2013; Zhu, Albrecht et al. 2013; Bach, Sillero et al. 2014; Fortier, Roberts et al. 2014; Li, Hu et al. 2014; Li, Liu et al. 2014; Neveux, Yuen et al. 2014; Tian, Li et al. 2014; Valdez, Tocco et al. 2014; Venteris, Skaggs et al. 2014), and supercritical water gasification (SWG: higher than 374°C) producing fuel gases (Schumacher, Yanik et al. 2011; Onwudili, Lea-Langton et al. 2013; Bagnoud-Velásquez, Brandenberger et al. 2014), as the main product. Other applications of HTP include hydrothermal hydrolysis (lower than 180°C) (Redwood, Orozco et al. 2012; Tsubaki, Oono et al. 2012; Xiao, Shi et al. 2013; Chimentão, Lorente et al. 2014; Kim, Lee et al. 2014), and wet torrefaction (180-250°C) (Chen, Ye et al. 2012; Bach, Tran et al. 2013; Reza, Yan et al. 2013; Bach, Tran et al. 2014), 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, Tran et al. 2013; Bach, Tran et al. 2014).

Fig. 1. Pressure-temperature (Moran, Shapiro 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.

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, Minowa et al. 2005; Knorr, Lukas et al. 2013; Elliott, Biller et al. 2015). Indeed, early continuous flow processes of HTL have been developed since the 1970–1980s (Elliott, Biller et al. 2015), including a laboratory work at Lawrence Berkeley Laboratory (Schaleger, Figueroa et al. 1982) and the Albany Biomass Liquefaction Experimental Facility (Thigpen 1982), both in the US, and the Hydrothermal Upgrading (HTU) plant (Goudriaan, van de Beld et al. 2001) in the Netherlands. However, only small scales of HTL have been demonstrated for short time periods (Elliott, Biller 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,

85 Biller et al. 2015). No clear winner in this area can be identified so far. There was a claim that HTL
86 was being implemented commercially to convert turkey waste to oil by Changing World Technologies
87 (Prapaiwatcharapan, Sunphorka et al. 2015), but the company went bankrupt and its RES plant in
88 Carthage has been transferred to Ridgeline Energy Services, a Canadian firm (Hacker 2013). Despite of
89 this fact, many recent studies have reported results from their investigation into the area of HTL of
90 biomass. This is perhaps due to the importance and potential of the HTL in biorefinery, producing
91 chemicals and biofuels from plant biomass. The work reported in this paper was carried out to identify
92 the key challenges and solutions for sustainable production of chemicals and biofuels from wet biomass
93 via HTL.

94 **2. Hot compressed water as reaction medium**

95 Water in standard conditions (25°C and 0.1 MPa) has a dielectric constant of 78, being a polar
96 solvent not suitable for organic compounds, mostly non-polar. However, in the region near the critical
97 point (374°C, 22.1 MPa) water acts as a non-polar solvent, being an extremely effective reaction
98 medium for organics. It is because, the density of water in liquid phase decreases with increasing
99 temperature. This change in the density correlates with other properties of water such as solvation
100 power, degree of hydrogen bonding, polarity, dielectric strength, molecular diffusivity, and viscosity.
101 For example, as shown in Fig. 1 and Table 1, the dielectric constant of water is dramatically decreased
102 as the temperature increases. The dielectric behaviour of 200°C water is similar to that of ambient
103 methanol, 300°C water is similar to ambient acetone, 370°C water is similar to methylene chloride, and
104 50°C water is similar to ambient hexane (James 2012).

105 Another interesting property of hot compressed water is its ion product. The ion product has a
106 maximum at around 250°C under saturation vapor pressure. When exceeding the critical point it drops
107 sharply. Overall, depending on the temperature and pressure hydrothermal media may support either
108 ionic or free radical reactions. At high densities below the critical temperature or in supercritical water
109 (SCW) at very high pressures, ionic reactions dominate. At high temperatures and low densities, free-

radical reactions are superior. Higher temperature reactions reduce char formation, but free radicals promote the formation of coke. On the other hand, the solubility of inorganic compounds, mostly polar, in ambient and hot compressed water is totally different from organics. As can be seen in Table 1, the solubility of inorganic compounds is very high in ambient water, but almost zero in SCW.

Table 1. Some physical properties of ambient and supercritical water, extracted from (James 2012)

Properties	Ambient water	Supercritical water
Dielectric constant	78	< 5
Solubility of organic compounds	Very low	Fully miscible
Solubility of inorganic compounds	Very high	≈ 0
Density (g.cm^{-3})	1	0.2-0.9

115

116 3. Key challenges and solutions

The challenges are various, including corrosion, energy and conversion efficiency, slurry feeding, product separation, biocrude stabilization, water management, and process cost (Crocker ; Peterson, Vogel et al. 2008; Kruse, Funke et al. 2013; Tekin, Karagöz et al. 2014). However, the major reactor engineering challenges are 1) corrosion; 2) precipitation of inorganic salts; and 3) char and coke formation (Calzavara, Jousset-Dubien et al. 2005; Matsumura, Minowa et al. 2005; Peterson, Vogel et al. 2008; Knorr, Lukas et al. 2013; Dărbăban, Rosendahl et al. 2015; Elliott, Biller et al. 2015). Among these, char and coke formation remains the most critical for biomass HTL. It is because HTL is working in sub-critical water conditions. The corrosion problem for HTL is much less serious than for SWG. More importantly, thanks to the technological advancements in metallurgy, it is possible to design and manufacture a suitable alloy that can stand and work effectively in hostile environments as such of hot compressed water or hydrothermal media (HM) once the reaction conditions are defined (Marrone and Hong 2009). Furthermore, the solubility of most inorganic salts only starts decreasing at the critical point of water, 374°C (Peterson, Vogel et al. 2008). Since HTL works in sub-critical water

130 conditions the problem of salt precipitation is virtually minimized. And if a HTL reactor is capable of
131 tolerating char and coke particles, it should also be able so for precipitated salt particles since salt
132 particles formed by nucleation are normally much smaller than char particles in size.

133 The problem associated with char and coke formation is common to HTL. Char comes from
134 incompletely converted biomass solids, while coke is resulted from further thermal decomposition of
135 biooil formed during HTL (Wang, Mourant et al. 2013). Both are unwanted for HTL since they are
136 directly responsible for the lower oil yields of the process and may block plug flow reactors after
137 several hours of running. Catalysts can be used to minimize the formation of these unwanted products
138 (Calzavara, Jousset-Dubien et al. 2005; Matsumura, Minowa et al. 2005; Zhang, Chen et al. 2013).
139 However, their application to HTL processes is limited due to the harsh conditions of HM and the cost
140 of catalysts used. Catalyst recovery is possible but may also be very challenging. Alternatively, the
141 problem can be minimized via fast heating, by which the biocrude yield is maximized (Zhang, von
142 Keitz et al. 2009; Akhtar and Amin 2011; Bach, Sillero et al. 2014; Brand, Hardi et al. 2014). In fact,
143 the effect of fast heating on char and coke minimization has been noticed from an earlier study (Modell
144 1985), in which Modell reported that no solid residue was observed from the experiment of introducing
145 small marble wood particles (3x0.5mm) into an autoclave reactor loaded with water and preheated to
146 377°C. Later, a number of studies demonstrated the importance of heating rate in improving the HTL
147 biocrude yield (Zhang, von Keitz et al. 2009; Akhtar and Amin 2011; Brand, Hardi et al. 2014). Brand
148 et al. (Brand, Hardi et al. 2014) indicated that, similar to fast pyrolysis, HTL consists of beneficial
149 primary reactions (pyrolytic & hydrolytic degradation) and non-beneficial secondary reactions i.e.
150 recombination and secondary cracking. In the case of slow heating, biomass undergoes step-by-step
151 hydrolytic degradation, pyrolytic degradation and, if elevated temperatures are applied, recombination
152 and secondary cracking reactions. Residence time and cooling rate would have marginal influence on
153 conversion due to the long temperature ramping period. When the heating rate increased, biomass is
154 instantaneously heated to the desired temperature, which would lead to simultaneous hydrolytic and

pyrolytic cleavage. Dominance of either pathway depends on the final temperature. In the case of a high final desired temperature, a long residence time will lead to recombination of liquid intermediates and secondary cracking. In this case, the cooling rate will have marginal influence on conversion because the system would reach a quasi-equilibrium state. On the other hand, the cooling rate can have an impact on biomass conversion under low final temperature and short residence time conditions. A slow cooling process will prolong the time period at a reactive temperature, i.e. decomposition can last slightly longer. Therefore, the maximum biocrude yield would be obtained by a combination of fast heating rates, high final temperatures and immediate quenching of the products (Brand, Hardi et al. 2014). In addition, heating rate also has strong effects on product characteristics including the fuel properties and functional groups of the products (Brand, Hardi et al. 2014), which are important for further applications and upgrading of the biocrude. This is in agreement with an earlier study (Ikushima, Hatakeda et al. 2002) in organic chemistry synthesis using a micro reaction system with a T mixer offering very high heating rates (700K/s), which claimed to achieve nearly 100% yield and 100% selectivity for *ε-caprolactam* production by *Beckmann* rearrangement of *cyclohexanone oxime* at reaction times shorter than 1 s. However, to apply such a micro reaction system for biomass HTL is not possible, just because the risk of reactor blockage by the solid particles in the system will be extremely high. So, as suggested by Matsumura et al. (Matsumura, Minowa et al. 2005), “*for continuously operated HTL plants, unusual process and reactor technology will be required to cope with fouling and necessary heating rates*”.

On the other hand, because of the need to improve the process economy (Knorr, Lukas et al. 2013; Zhu, Biddy et al. 2014; Dărbăban, Rosendahl et al. 2015; Elliott, Biller et al. 2015), it may be argued that high-pressure feeding systems for more concentrated biomass slurries has still remained a process engineering challenge for HTL (Peterson, Vogel et al. 2008; Elliott, Biller et al. 2015). This may be true, but just in laboratory conditions. High-pressure pumping biomass slurries was reported accomplished at the laboratory scale at several places, but in all cases the slurry concentration was

180 limited to 20 wt. % (Peterson, Vogel et al. 2008; Berglin, Enderlin et al. 2012; Knorr, Lukas et al.
181 2013; Zhu, Biddy et al. 2014; Elliott, Biller et al. 2015). However, since 1987 the University of
182 Arizona has developed a method of high-pressure pumping concentrated, viscous biomass slurries,
183 characteristic in biomass direct liquefaction systems (White and Wolf 1987). It claimed to be capable
184 of pumping solid slurries as high as 60 wt. % wood flour, as compared to only 10-20 wt. % wood flour
185 in conventional systems (White and Wolf 1987; White, Coates et al. 1996). A recent investigation
186 indicated that 36.6 wt% for biomass slurry has been recommended to ensure the HTL process
187 economically feasible and this capacity has been confirmed achievable by the industry (Harris Group
188 Inc.) (Knorr, Lukas et al. 2013). In addition, an earlier study suggested that the maximum viscosity of a
189 pumpable slurry is 1.0 Pa·s (Jazrawi, Biller et al. 2015), while another demonstrated that the solid
190 loading in the hydrochar-water slurry of 0.7 Pa·s increased to nearly 35 wt. % (He, Park et al. 2009).
191 These suggest that the feeding challenge at the laboratory scale can be solved by pretreatment of
192 biomass via HTC, producing hydrochar.

193 **4. Reactor developments and discussions**

194 Although it is not possible to apply the micro reaction system with a T mixer, studied by Ikushima
195 (Ikushima, Hatakeda et al. 2002), for fast HTL of biomass, an important lesson learnt from this study
196 is that very fast heating for the reactants can be achieved by heat transfer via convection, mixing of two
197 fluid flows: preheated pure water and non-preheated reactant flow. Many different reactor designs with
198 different heating methods for biomass HTL at laboratory scales have recently been summarized and
199 compared (Brand, Hardi et al. 2014). However, all of the reported reactors are based on the batch
200 reactor design, in which the heat transfer from the external heat source to the reactant fluid is taking
201 place though the reactor wall via conduction. Therefore, it is not possible to achieve very high heating
202 rates needed for fast HTL of biomass at industrial scales. Two-stage processes and techno-economic
203 assessments for different continuous process configurations in different industrial scenarios have also
204 been reported (Knorr, Lukas et al. 2013; Zhu, Biddy et al. 2014; Elliott, Biller et al. 2015; Jazrawi,

Biller et al. 2015; Prapaiwatcharapan, Sunphorka et al. 2015). However, the assessed processes were designed based on the CSTR (continuous stirring tank reactor) concept for biomass HTL reactors. This type of reactor is well-known and not capable of coping with fouling and necessary heating and cooling rates, which are required for continuously operated fast HTL plants. Therefore, it is critical to develop a tubular (plug-flow) reactor, for fast HTL of biomass, with design criteria as below:

- Instantaneous strong and uniform mixing of two fluid flows (the larger flow is pure water and preheated) of big difference in volumetric flow rate, to aid in achieving very fast heating for the smaller flow containing biomass particles;
- Short average residence time combined with a narrow residence time distribution, to minimize coke formation;
- Minimal heating of the slurry stream of biomass in water prior to the reactor, followed by immediate and rapid heating of the slurry stream within the reactor, to prevent side reactions;
- Strong net downstream flow/eddies for the rapid transport of product particles out of the reactor, to prevent particle accumulation within the reactor and to minimize subsequent coke particle formation.

Fig 2. Conceptual process diagram for fast HTL of biomass

For such a reactor, a process with fast cooling of the product stream is straightforward to design as demonstrated in Fig. 2. In addition, it is possible to introduce organic liquids such as ethanol into the downstream of the reactor in order to 1) make the biocrude more stable and less viscous by blocking the reactive functional groups (Brand, Hardi et al. 2014) and 2) cool down the product stream and quench unwanted further reactions (recombination and secondary cracking (Brand, Hardi et al. 2014)). Given the reactor and process are properly designed and developed, it is reasonable to expect that optimum combinations of high heating and cooling rates with reaction temperature and time for biomass HTL would result in high yields and high selectivity for biocrude. The economic benefit of achieving high oil yield is obvious. The high selectivity, demonstrated as Curves B and C in Fig. 3, can be translated to a smaller number of major organic compounds present in the biocrude (Curve A, Fig. 3) that normally contains thousands different compounds, and thus makes it easier or more economically to utilizing or upgrading the biocrude.

Fig. 3. Molecular weight distributions for biocrude for different reaction conditions

By optimizing the process parameters (heating, cooling, reaction temperature and time), production of biocrude containing desired compounds would be possible. Catalyst addition upstream or during the process is also possible, for further improvements of biocrude quality. The most optimistic case is anticipated to offer the opportunity to achieve a single-step process for production

of biocrude analogous to petroleum crude, considering that today biocrude is not a petroleum analog (Elliott, Biller et al. 2015).

5. Conclusion

Although HTL is a promising technology for directly converting wet plant biomass to chemical and liquid biofuels, engineering challenges remain obstacles to its industrial applications, of which the most critical challenges can be divided into three groups in connection with 1) corrosion; 2) char and coke formation; and 3) precipitation of inorganic salts. Efforts were made to overcome the problems individually. However, none was able to cope with the problems simultaneously, in a single reaction system. It has been identified and reconfirmed that the key challenge and its solution for HTL is to develop a plug flow reactor for a continuously operated HTL plants and for such a plant unusual process and reactor technology will be required to cope with fouling and necessary heating rates.

Acknowledgement

This work was financially supported by the Department of Energy and Process Engineering, Norwegian University of Science and Technology, which is gratefully acknowledged.

References

1. Akhtar, J. and N. A. S. Amin (2011). "A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass." *Renewable and Sustainable Energy Reviews* **15**(3): 1615-1624.
2. Anastasakis, K. and A. B. Ross (2011). "Hydrothermal liquefaction of the brown macro-alga *Laminaria Saccharina*: Effect of reaction conditions on product distribution and composition." *Bioresource Technology* **102**(7): 4876-4883.
3. Archer, D. G. and P. Wang (1990). "The Dielectric Constant of Water and Debye H $\ddot{A}$ ckel Limiting Law Slopes." *Journal of Physical and Chemical Reference Data* **19**(2): 371-411.
4. Bach, Q.-V., M. V. Sillero, et al. (2014). "Fast hydrothermal liquefaction of a Norwegian macro-alga: Screening tests." *Algal Research* **6**(B): 271-276.

5. Bach, Q.-V., K.-Q. Tran, et al. (2014). "Effects of wet torrefaction on reactivity and kinetics of wood under air combustion conditions." *Fuel* **137**(0): 375-383.
6. Bach, Q. V., K.-Q. Tran, et al. (2013). "A comparative assessment of wet torrefaction." *Energy & Fuels* **27**(11): 6743-6753.
7. Bagnoud-Velásquez, M., M. Brandenberger, et al. (2014). "Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling." *Catalysis Today* **223**(0): 35-43.
8. Berglin, E. J., C. W. Enderlin, et al. (2012). "Review and assessment of commercial vendors/options for feeding and pumping biomass slurries for hydrothermal liquefaction." *Review and Assessment of Commercial Vendors/Options for Feeding and Pumping Biomass Slurries for Hydrothermal Liquefaction*.
9. Brand, S., F. Hardi, et al. (2014). "Effect of heating rate on biomass liquefaction: Differences between subcritical water and supercritical ethanol." *Energy* **68**(0): 420-427.
10. Calzavara, Y., C. Jousot-Dubien, et al. (2005). "Evaluation of biomass gasification in supercritical water process for hydrogen production." *Energy Conversion and Management* **46**(4): 615-631.
11. Chen, W.-H., S.-C. Ye, et al. (2012). "Hydrothermal carbonization of sugarcane bagasse via wet torrefaction in association with microwave heating." *Bioresource Technology* **118**(0): 195-203.
12. Chimentão, R. J., E. Lorente, et al. (2014). "Hydrolysis of dilute acid-pretreated cellulose under mild hydrothermal conditions." *Carbohydrate Polymers* **111**(0): 116-124.
13. Crocker, M. *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*, Royal Society of Chemistry: 192.
14. Dărbăban, I. M., L. A. Rosendahl, et al. (2015). "Pretreatment methods to obtain pumpable high solid loading wood–water slurries for continuous hydrothermal liquefaction systems." *Biomass and Bioenergy* **81**: 437-443.
15. Elliott, D. C., P. Biller, et al. (2015). "Hydrothermal liquefaction of biomass: Developments from batch to continuous process." *Bioresource Technology* **178**: 147-156.
16. Elliott, D. C., T. R. Hart, et al. (2013). "Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor." *Algal Research* **2**(4): 445-454.
17. Fortier, M.-O. P., G. W. Roberts, et al. (2014). "Life cycle assessment of bio-jet fuel from hydrothermal liquefaction of microalgae." *Applied Energy* **122**(0): 73-82.
18. Goudriaan, F., B. van de Beld, et al. (2001). "Thermal efficiency of the HTU process for biomass liquefaction." *Progress in Thermochemical Biomass Conversion*: 1312-1325.

19. Hacker, J. (2013). "Canadian firm acquires Carthage RES plant."
from <http://www.carthagepress.com/article/20130416/NEWS/130419181/1001/NEWS>.
20. He, W., C. S. Park, et al. (2009). "Rheological study of comingled biomass and coal slurries with hydrothermal pretreatment." *Energy and Fuels* **23**(10): 4763-4767.
21. Heilmann, S. M., H. T. Davis, et al. (2010). "Hydrothermal carbonization of microalgae." *Biomass and Bioenergy* **34**(6): 875-882.
22. Ikushima, Y., K. Hatakeda, et al. (2002). "Innovation in a chemical reaction process using a supercritical water microreaction system: Environmentally friendly production of ϵ -caprolactam." *Chemical Communications*(19): 2208-2209.
23. James, W. L., Ed. (2012). *Advanced Biofuels and Bioproducts*, Springer.
24. Jazrawi, C., P. Biller, et al. (2015). "Two-stage hydrothermal liquefaction of a high-protein microalga." *Algal Research* **8**: 15-22.
25. Kim, D.-H., S.-B. Lee, et al. (2014). "Production of reducing sugar from *Enteromorpha intestinalis* by hydrothermal and enzymatic hydrolysis." *Bioresource Technology* **161**(0): 348-353.
26. Knorr, D., J. Lukas, et al. (2013). "Production of Advanced Biofuels via Liquefaction - Hydrothermal Liquefaction Reactor Design: April 5, 2013." *Production of Advanced Biofuels via Liquefaction - Hydrothermal Liquefaction Reactor Design*.
27. Kruse, A., A. Funke, et al. (2013). "Hydrothermal conversion of biomass to fuels and energetic materials." *Current Opinion in Chemical Biology* **17**(3): 515-521.
28. Li, H., J. Hu, et al. (2014). "Insight into the effect of hydrogenation on efficiency of hydrothermal liquefaction and physico-chemical properties of biocrude oil." *Bioresource Technology* **163**(0): 143-151.
29. Li, H., Z. Liu, et al. (2014). "Conversion efficiency and oil quality of low-lipid high-protein and high-lipid low-protein microalgae via hydrothermal liquefaction." *Bioresource Technology* **154**(0): 322-329.
30. Libra, J. A., K. S. Ro, et al. (2011). "Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis." *Biofuels* **2**(1): 71-106.
31. Liu, X., B. Saydah, et al. (2013). "Pilot-scale data provide enhanced estimates of the life cycle energy and emissions profile of algae biofuels produced via hydrothermal liquefaction." *Bioresource Technology* **148**(0): 163-171.

32. Marrone, P. A. and G. T. Hong (2009). "Corrosion control methods in supercritical water oxidation and gasification processes." *The Journal of Supercritical Fluids* **51**(2): 83-103.
33. Matsumura, Y., T. Minowa, et al. (2005). "Biomass gasification in near- and super-critical water: Status and prospects." *Biomass and Bioenergy* **29**(4): 269-292.
34. Modell, M. (1985). *Gasification and liquefaction of forest products in supercritical water. Fundamentals of Thermochemical Biomass Conversion*. Amsterdam, Elsevier: 95-119.
35. Moran, M. J., H. N. Shapiro, et al. (2011). *Fundamentals of Engineering Thermodynamics*, Wiley.
36. Neveux, N., A. K. L. Yuen, et al. (2014). "Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae." *Bioresource Technology* **155**(0): 334-341.
37. Onwudili, J. A., A. R. Lea-Langton, et al. (2013). "Catalytic hydrothermal gasification of algae for hydrogen production: Composition of reaction products and potential for nutrient recycling." *Bioresource Technology* **127**(0): 72-80.
38. Peterson, A. A., F. Vogel, et al. (2008). "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies." *Energy & Environmental Science* **1**(1): 32-65.
39. Pham, M., L. Schideman, et al. (2013). "Effects of hydrothermal liquefaction on the fate of bioactive contaminants in manure and algal feedstocks." *Bioresource Technology* **149**(0): 126-135.
40. Prapaiwatcharapan, K., S. Sunphorka, et al. (2015). "Single- and two-step hydrothermal liquefaction of microalgae in a semi-continuous reactor: Effect of the operating parameters." *Bioresource Technology* **191**: 426-432.
41. Redwood, M. D., R. L. Orozco, et al. (2012). "An integrated biohydrogen refinery: Synergy of photofermentation, extractive fermentation and hydrothermal hydrolysis of food wastes." *Bioresource Technology* **119**(0): 384-392.
42. Reza, M. T., W. Yan, et al. (2013). "Reaction kinetics of hydrothermal carbonization of loblolly pine." *Bioresource Technology* **139**(0): 161-169.
43. Schaleger, L. L., C. Figueroa, et al. (1982). *Direct Liquefaction of Biomass: Results from Operation of Continuous Bench-Scale Unit in Liquefaction of Water Slurries of Douglas Fir Wood*. Biotechnology Bioengineering Symposium.
44. Schumacher, M., J. Yanik, et al. (2011). "Hydrothermal conversion of seaweeds in a batch autoclave." *The Journal of Supercritical Fluids* **58**(1): 131-135.

45. Singh, R., T. Bhaskar, et al. "Effect of solvent on the hydrothermal liquefaction of macro algae *Ulva fasciata*." *Process Safety and Environmental Protection*(0).
46. Tekin, K., S. Karagöz, et al. (2014). "A review of hydrothermal biomass processing." *Renewable and Sustainable Energy Reviews* **40**(0): 673-687.
47. Thigpen, P. L. (1982). Final Report: An Investigation of Liquefaction of Wood at the Biomass Liquefaction Facility, Albany, Oregon, Battelle Pacific Northwest Laboratories, Department of Energy, Wheelabrator Cleanfuel Corporation.
48. Tian, C., B. Li, et al. (2014). "Hydrothermal liquefaction for algal biorefinery: A critical review." *Renewable and Sustainable Energy Reviews* **38**(0): 933-950.
49. Toor, S. S., H. Reddy, et al. (2013). "Hydrothermal liquefaction of *Spirulina* and *Nannochloropsis salina* under subcritical and supercritical water conditions." *Bioresource Technology* **131**(0): 413-419.
50. Tsubaki, S., K. Oono, et al. (2012). "Microwave-assisted hydrothermal hydrolysis of cellobiose and effects of additions of halide salts." *Bioresource Technology* **123**(0): 703-706.
51. Valdez, P. J., V. J. Tocco, et al. (2014). "A general kinetic model for the hydrothermal liquefaction of microalgae." *Bioresource Technology* **163**(0): 123-127.
52. Vardon, D. R., B. K. Sharma, et al. (2011). "Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge." *Bioresource Technology* **102**(17): 8295-8303.
53. Venteris, E. R., R. L. Skaggs, et al. (2014). "A national-scale comparison of resource and nutrient demands for algae-based biofuel production by lipid extraction and hydrothermal liquefaction." *Biomass and Bioenergy* **64**(0): 276-290.
54. Wang, Y., D. Mourant, et al. (2013). "Formation of coke during the pyrolysis of bio-oil." *Fuel* **108**(0): 439-444.
55. White, D. H., W. E. Coates, et al. (1996). "Conversion of cotton plant and cotton gin residues to fuels by the extruder feeder liquefaction process." *Bioresource Technology* **56**(1): 117-123.
56. White, D. H. and D. Wolf (1987). Continuous Extruder-Feeder for Reactor Systems for Biomass Fuels Processing. Symposium Papers - Energy from Biomass and Wastes.
57. Xiao, L.-P., Z.-J. Shi, et al. (2013). "Hydrothermal treatment and enzymatic hydrolysis of *Tamarix ramosissima*: Evaluation of the process as a conversion method in a biorefinery concept." *Bioresource Technology* **135**(0): 73-81.
58. Zhang, B., M. von Keitz, et al. (2009). "Thermochemical liquefaction of high-diversity grassland perennials." *Journal of Analytical and Applied Pyrolysis* **84**(1): 18-24.

- 412 59. Zhang, J., W.-T. Chen, et al. (2013). "Hydrothermal liquefaction of *Chlorella pyrenoidosa* in
413 sub- and supercritical ethanol with heterogeneous catalysts." *Bioresource Technology* **133**: 389-
414 397.
- 415 60. Zhou, D., L. Zhang, et al. (2010). "Hydrothermal Liquefaction of Macroalgae *Enteromorpha*
416 *prolifera* to Bio-oil." *Energy & Fuels* **24**(7): 4054-4061.
- 417 61. Zhu, Y., K. O. Albrecht, et al. (2013). "Development of hydrothermal liquefaction and
418 upgrading technologies for lipid-extracted algae conversion to liquid fuels." *Algal Research*
419 **2**(4): 455-464.
- 420 62. Zhu, Y., M. J. Biddy, et al. (2014). "Techno-economic analysis of liquid fuel production from
421 woody biomass via hydrothermal liquefaction (HTL) and upgrading." *Applied Energy* **129**:
422 384-394.
- 423
424