Hydrothermal Liquefaction Of Biomass – An Alternate Sustainable Energy

Devika R, Subathra M

Abstract: Hydrothermal liquefaction (HTL) is a thermal depolymerization involving homogenous catalysts to improve the quality of products depending on processing conditions. Any biomass can be converted into bio oil irrespective of compositions which influenced the quality of product. The major parameter has effect on the reaction kinetics and energy inputs required for product production. Biofuels through HTL are devoid of carbon emission during combustion and doesn't emit harmful gases like ammonia, NOx, Sox etc. HTL process consumes 10-15% of energy from the feed stock biomass yielding 85-90 % energy. The bio oil generated through HTL can be used for heavy engines or upgraded to obtain diesel, gasoline or jet fuels.

Key Words: Polymerization, decomposition, pyrolysis, emission, biofuel, catalysts, solvent, cellulose, lignin, biomass.

1 INTRODUCTION

Energy demand in the rapid growth rate of urbanization in the past few decades has become a public threat [1,2]. Since 2010, production of biofuel (bioethanol, biodiesel) has been advanced and listed under alternate source of energy from lignocellulosic materials. Biomass includes agricultural crop plants, algae, aquatic plants, wood wastes, food wastes, animal wastes, municipal wastes etc. [3]. Evidences of various researches on biomass has been carried in few decades SpirulinaSps.[4], Cladophora [5,6,7], Oedogonium [8], Algal wastes [9], Porphyridium [10], Taihucyanophyta [11], Pine saw dust [12], Microcystis [13], Sargassum [14], Botryococcusbraunii [15], Fucusvesiculosus [16], Daturastramonium [17], ChorellaSps.[18], Synechococcus [19], Naanocholrophosissalina [20]. Several experimental reports proved that the production of biocrude from biomass highly dependent on the composition and chemical properties of biomass [21,22,23] and other parameters which influences the final liquefaction are temperature, biomass heating, size of biomass, residue time, types of solvents, selection of catalysts, decomposition mechanisms etc. [1,24]. Hydrothermal liquefaction (HTL) processes yielded value added chemical compounds such as esters, branched aliphatic groups, aromatic compounds, carboxylic acids and phenolic derivatives and nitrogen based ring structures [1,23,25]. The reaction mechanism of biomass in HTL process includes hydrolysis (biomass broken into fragments) followed by dehydration, dehydrogenation, deoxygenation and decarboxylation [1,26,27,28]. Desired aromatic compounds (phenolic derivatives) were obtained through conventional operating temperature methods through HTL process using wet and dry biomass [29]. The current HTL technologies was scaled up for decades with sewage sludge [30], petroleum [31], algae [32,33,34,35].

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2 MECHANISM OF HYDROTHERMAL LIQUEFACTION

The three major pathways of HTL are depolymerisation, decomposition and recombination [36] since the biomass is a complex compound having carbohydrates, lignin, cellulose, lipids, proteins etc. [37,38]. Depolymerization involves sequential dissolving of the macromolecules into shorter chain hydrocarbons depending on the physical and chemical properties in the presence of water [39,40].Monosaccharides are formed from hemicelluloses or cellulose [41,42], methoxyphenol derivatives from lignin [43] proteins degrades to amino acids [44] and lipids to fatty acids / monoglycerides, respectively. Evidences on the research works with monomers showed better efficiency and valuable interactive effects instead of complex compounds (eg. Glucose-glutamic acid and guaiacol-linleic acid conversion and amide formation) [45,46,47]. The steps involved in decomposition processes are loss of CO_2 (decarboxylation), removal of amino acids (deamination), removal of oxygen in the form of water and CO_2, respectively and results in monomers, oligmers, furfurals, glycoaldehydes, phenols, organic acids, organic molecules and they are all readily soluble in water [48,49,50]. The third step depends on the availability of hydrogen compound [36] or excess presence of free radicals and therefore results in recombination or repolymerization to large molecular weight chared of coke formation [51]. The ulktimate target of this HTL is to convert the biomass to bio-crude which utilizes 10-15% of energy and efficient in producing 85-90% energy yield and proved to be an alternate commercial biofuel [52,53]. The resultant products obtained through HTL are phenol [54], cholesterol and cholestene [55], palmitic acid [56], octanoic acid [57], hexadecanoic acid [58], naphthalene [59], fluorine [60] indoles [54], amides [61], esters [62], alcohols [63], furans [64]. Biocrude yield of proteins was 19.91 (wt.%), hemicelluloses (5.27 wt.%), cellulose 14.23 (wt.%) through model component mixture in HTL [65] and it also proved that the model feedstock showed solid residues yield higher than the predicted value (8.54 wt.% - predicted value and 11.09 wt.% of actual yield). Similar result was reported which had 0.9 wt.% as predicted value and 4.8 wt.% of solid residues as yield [66] and this variation of yield might be due to the organic solvents used in the process [67].

3 GC-MS ANALYSIS OF HTL COMPOUNDS

GC-MS analysis of bio oils reported eleven different chemical groups such as esters, amide, amines, diketopiperazine, furan, phenol, acid, hydrocarbon, ketone, aldehydes etc., [65,68,69]. Diketopiperazine was produced in a higher volume from protein biocrude raw materials including 3,6-diisopropylpiperazine-2,5-dione, 3,6-bis (2-methylpropyl)-2,5-piperazinedione and pyrrolo-pyrazine-1,4 dione [70,71,72]. The two major chemical groups from lipids are fatty acids and esters under GC_MS analysisand the representative chemical compounds were 2,3 – dihydroxypropyl – 9,12 octadecadienoic ester, 9,12 – octadecadienoic acid, buyyl9,12 – octadecedienoate etc. [73,74] and the production dependent on temperature and residue time [75,76]. It was evident that the thermal stability of fatty acid and esters as (18 : 2 carbon chain) [65]. Identified cellulosic compounds were in the form of aldehyses and ketones [65] where aldehydes as furfural derivatives as 5- hydro-xymethyl – furfural (5-HMP) and ketone compounds as 3-methyl-1,2, cyclopentane etc. Similar representation in the case of hemicelluloses was observed (aldehyde 6.5 mg/g) and keetone (1.3mg/g) [75]. The chemical decomposition of xylose resuled as phenolic derivatives such as 4-hydroxy-3methoxy-benzene proponol, vanillin, apocynin,guaiacol and cresol etc. [79,80]. The biocrude under GC-MS reported majority of compounds of C_6 – C_{21} with various functional groups (aldehydes, phenolic, ketonic etc.) [81,82].

4 PROCESS CONDITIONS AND PRODUCT PRODUCTION

Recently, enormous researches pertaining to hydrothermal liquefaction under different parameters and techniques has been reported with wet and dry biomasses. Bio oil derived as like conventional gasoline [83] and from dry biomass resembled as pyrolysis oil [84]. Barley straw (batch culture) at 280 – 400^{0}C and 350 bar pressure produced bio oil with less amount of phenols and acids, whereas at temperature 300^{0}C and 90 bar pressure produced more of phenol and less carboxylic compounds [29,85]. Hydrothermal liquefaction of Chorellapyrenoidosa at 280^{0}C (temperature) and 25 MPa (pressure) reported a best yield of 57.3 wt.% biocrude production [86] and similar research on Chorellapyrenoidosa at 300^{0}C yielded zeolite Ce / H2SM-5 and resembled bio oil with high potential and efficiency [87]. Research pertaining to high heating value [HHV] products is represented in the Table 1. Hydrothermal liquefaction process of Nannochloropsisgaditanayielded 47.6% of carbon, 7.5% hydrogen, 6.9% nitrogen, 25.1% oxygen, 0.5% sulphur and 12.4% ash [99] and Nannochoropsisoceana yielded 50.3 % carbon, 7.6% hydrogen, 7.3% nitrogen, 0.3% sulphur and lacked oxygen and ash content during the process, respectively [5]. Derbesia registered 29.2% carbon, 27.4 oxygen, 34.7% ash with 12.4 MJ/Kg of HHV [100].

Table: 1 *Literature pertaining high heating value (HHV) product*

S.No	Feed	Process condition Temperature / Pressure	HHV MJ/Kg	Reference
1	Jatrophacurcas cake	250 ^{0}C / 4.5 MPa	25.01	Alhassan et al., [35]
2	Feedstock - Indianapolis	260-320^{0}C / 1 MPa	33.3	Chen et al., [18]
3	TetraselmisSps, SpirulinaSps.	300 -350^{0}C / 30 bar	40	Eboibi [90]
4	Wheat straw	350^{0}C /200 bar	28	Patil et al., [40]
5	Aspen wood and gluerol mixture	400^{0}C / 300 bar	39	Pederson and Rosendahl [45]
6	Nannochloropsis Sps., PavlovaSps, IsochrysisSps.	250 - 350^{0}C / 35 Psi	37	Shakya et al., [90]
7	Nannochloropsis gaditana, ChorellaSps.,	300^{0}C / 200 Psi	34.5	Reddy et al., [91]
8	Beach wood	250 - 350^{0}C / 4-16.5 MPa	23.81	Tekin et al., [92]
9	ScenedesmusSps.,, Spirulina	300 - 450^{0}C / 10 -12 MPa	35-37	Vardon et al., [33]
10	Spent coffee ground	200 - 300^{0}C / 0.5 – 2 MPa	31	Yang et al., [64]
11	Seaweed (Sugar kelp)	-	14.46	Bach et al., [93]
12	Posidoniaoceanica	-	12.82	Plis et al., [94]
13	AlmeriensisSps.	-	17.6	DiazRay et al., [95]
14	MougeotiaSps.	-	25.4	Sharasa et al., [90]
15	ChorellaSps.	-	18.59	Phukar et al., [97]
16	Laurusnobilis	-	19.77	Erbas and Alma [98]

5 CONCLUSION

The present overview of HTL process proves that the product obtained through HTL yields 35-39 MJ/Kg heating value, devoid of carbon emission, NOx, Sox during combustion. The energy yield was 85-90% and can be employed in heavy engines, jet engines, bio diesel etc. and they are storage stable. Therefore, HTL has been considered as the most promising path for sustainable bio oil products.

6 REFERENCE

[1] A.R.K. Gollakota, N. Kishore and S. Gu, “A review on hydrothermal liquefaction of biomass,” Renewable and Sustainable Energy Reviews, vol. 81, pp. 1378–1392, Jan. 2018.

[2] Maxime Deniel, Geert Haarlemmer, Anne Roubaud, Elsa Weiss-Hortala, Jacques Fages, “Energy Valorisation of Food Processing Residues and Model Compounds by Hydrothermal

Liquefaction- Review," Renewable and Sustainable Energy Reviews, vol. 54, pp. 1632-1652, 2016.
[3] P.L. Thigpen and B.W.L. Jr, "Liquid fuels from wood by continuous operation of the Albany, Oregon biomass liquefaction facility," 1982.
[4] D.R. Vardon, B.K. Sharma, J. Scott, G. Yu, Z. Wang, L.Schideman, Y. Zhang, "Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge," Bioresource Technology, vol. 102, no. 17, pp. 8295–8303, Sep. 2011.
[5] M.P. Caporgno, J. Pruvost, J. Legrand, O. Lepine, M. Tazerout, and C. Bengoa, "Hydrothermal liquefaction of Nannochloropsisoceanica in different solvents," Bioresource Technology, vol. 214, pp. 404–410, Aug. 2016.
[6] T.H. Pederson, L.A. Rosendatl, "Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems," Biomass Bioenergy, vol. 83, pp. 206-215, 2015.
[7] A. Plis, J. Lasek, A. Skawińska and J. Zuwała, "Thermochemical and kinetic analysis of the pyrolysis process in Cladophoraglomerata algae," Journal of Analytical and Applied Pyrolysis, vol. 115, pp. 166–174, Sep. 2015.
[8] L. Yang, L. Nazari, Z. Yuan, K. Corscadden, C. Charles Xu, and Q. Sophia He, "Hydrothermal liquefaction of spent coffee grounds in water medium for bio-oil production," Biomass and Bioenergy, vol. 86, pp. 191–198, Mar. 2016.
[9] W.T. Chen, Y. Zhang, J. Zhang, G. Yu, L.C. Schideman, P. Zhang, M. Minarick, "Hydrothermal liquefaction of mixed-culture algal biomass from wastewater treatment system into bio-crude oil," Bioresource Technology, vol. 152, pp. 130–139, Jan. 2014.
[10] S. Raikova, H. Smith-Baedorf, R. Brangrove, O. Barlow, F. Santomauro, J. Wagner, M.J. Allen, C.G. Bryan, D. Sapsdrof, C. Chuck, "Assessing hydrothermal liquefaction for the production of bio-oil and enhanced metal recovery from microalgae cultivated on acid mine drainage," Fuel Processing Technology, vol. 142, pp. 219–227, Feb. 2016.
[11] Guo Y, Yeh T, Song W, Xu D, Wang S,"A review of bio-oil production from hydrothermal liquefaction of algae," Renew Sustain Energy Rev, vol. 48, pp. 776–90, 2015.
[12] P. Nautiyal, K.A. Subramanian and M.G. Dastidar, "Production and characterization of biodiesel from algae," Fuel Processing Technology, vol. 120, pp. 79–88, Apr. 2014.
[13] Z. Hu, Y. Zheng, F. Yan, B. Xiao, and S. Liu, "Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): Product distribution and bio-oil characterization," Energy, vol. 52, pp. 119–125, Apr. 2013.
[14] S. Ceylan, Y. Topcu and Z. Ceylan, "Thermal behaviour and kinetics of alga Polysiphoniaelongata biomass during pyrolysis," Bioresource Technology, vol. 171, pp. 193–198, Nov. 2014.
[15] Y.Q. Liu, L.R.X. Lim, J. Wang, R. Yan and A. Mahakhant, "Investigation on Pyrolysis of Microalgae Botryococcusbraunii and Hapalosiphon sp.," Ind. Eng. Chem. Res., vol. 51, no. 31, pp. 10320–10326, Aug. 2012.
[16] A.B. Ross, J.M. Jones, M.L. Kubacki and T. Bridgeman, "Classification of macroalgae as fuel and its thermochemical behaviour," Bioresource Technology, vol. 99, no. 14, pp. 6494–6504, Sep. 2008.
[17] T. Aysu and H. Durak, "Thermochemical conversion of Daturastramonium L. by supercritical liquefaction and pyrolysis processes," The Journal of Supercritical Fluids, vol. 102, pp. 98–114, Jul. 2015.
[18] M.M. Phukan, R.S. Chutia, B.K. Konwar, and R. Kataki, "Microalgae Chlorella as a potential bio-energy feedstock," Applied Energy, vol. 88, no. 10, pp. 3307–3312, Oct. 2011.
[19] J. Wagner et al., "Co-production of bio-oil and propylene through the hydrothermal liquefaction of polyhydroxybutyrate producing cyanobacteria," Bioresource Technology, vol. 207, pp. 166–174, May 2016.
[20] S.S. Toor et al., "Hydrothermal liquefaction of Spirulina and Nannochloropsissalina under subcritical and supercritical water conditions," Bioresource Technology, vol. 131, pp. 413–419, Mar. 2013.
[21] S.S. Toor, L. Rosendahl, and A. Rudolf, "Hydrothermal liquefaction of biomass: A review of subcritical water technologies," Energy, vol. 36, no. 5, pp. 2328–2342, May 2011.
[22] J. Akhtar and N.A.S. Amin, "A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass," Renewable and Sustainable Energy Reviews, vol. 15, no. 3, pp. 1615–1624, Apr. 2011.
[23] A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, J. Michael J. Antal and J.W. Tester, "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies," Energy Environ. Sci., vol. 1, no. 1, pp. 32–65, Jul. 2008.
[24] K. Tekin, S. Karagöz, and S. Bektaş, "A review of hydrothermal biomass processing," Renewable and Sustainable Energy Reviews, vol. 40, pp. 673–687, Dec. 2014.
[25] P.E. Savage, "Algae Under Pressure and in Hot Water," Science, vol. 338, no. 6110, pp. 1039–1040, Nov. 2012.
[26] E. Chornet and R.P. Overend, "Biomass Liquefaction: An Overview," in Fundamentals of Thermochemical Biomass Conversion, Springer Netherlands, pp. 967–1002, 1985.
[27] M. Balat, "Mechanisms of Thermochemical Biomass Conversion Processes. Part 3: Reactions of Liquefaction," Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, vol. 30, no. 7, pp. 649–659, Mar. 2008.
[28] X.Z. Yuan, J.Y. Tong, G.M. Zeng, H. Li and W. Xie, "Comparative Studies of Products Obtained at Different Temperatures during Straw Liquefaction by Hot Compressed Water," Energy Fuels, vol. 23,

no. 6, pp. 3262–3267, Jun. 2009.
[29] Z. Zhu, L. Rosendahl, S. S. Toor, D. Yu, and G. Chen, “Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation,” Applied Energy, vol. 137, pp. 183–192, Jan. 2015.
[30] S. Itoh, A. Suzuki, T. Nakamura, and S. Yokoyama, “Production of heavy oil from sewage sludge by direct thermochemical liquefaction,” Desalination, vol. 98, no. 1, pp. 127–133, Sep. 1994.
[31] T. Minowa, S. Yokoyama, M. Kishimoto and T. Okakura, “Oil production from algal cells of Dunaliellatertiolecta by direct thermochemical liquefaction,” Fuel, vol. 74, no. 12, pp. 1735–1738, Dec. 1995.
[32] Y. Dote, S. Sawayama, S. Inoue, T. Minowa and S. Yokoyama, “Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction,” Fuel, vol. 73, no. 12, pp. 1855–1857, Dec. 1994.
[33] D.R. Vardon, B.K. Sharma, G.V. Blazina, K. Rajagopalan and T.J. Strathmann, “Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis,” Bioresour. Technol, vol. 109, pp. 178–187, Apr. 2012.
[34] L.G. Alba, C. Torri, C. Samori, J.J. Van der Spek, D. Fabbri, S.R.A. Kersten, D.W.F. Brilman, “Hydrothermal Treatment of microalgae; Evaluation of the process as Conversion Method in an Algae Biorefinery Concept,” Energy & Fuels, vol. 26, pp. 642–57, 2012
[35] S. Xiu, A. Shahbazi, V. Shirley and D. Cheng,“Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil,” J Anal Appl Pyrolysis, vol. 88, pp. 73–9, 2010.
[36] S. Sohail, L. Rosendahl, A. Rudolf, ” Hydrothermal liquefaction of biomass: a review of subcritical water technologies,” Energy, vol. 36, pp. 2328–42, 2011.
[37] P. McKendry, “Energy production from biomass (part 2): conversion technologies,” Bioresource Technology, vol. 83, no. 1, pp. 47–54, May 2002.
[38] P. Sigard Christensen, “Hydrothermal liquefaction of waste biomass – optimizing reaction parameters,” 2014.
[39] J. Jae, G.A.Tompsett, Y.C. Lin, T.R.Carlson, J. Shen, T.Zhang, B. Yang, C.E. Wyman, W.C. Conner and G.W. Huber, “Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis,” Energy Environ. Sci., vol. 3, no. 3, pp. 358–365, Mar. 2010.
[40] M. Zein, R. Winter, “Effect of temperature, pressure and lipid acyl chain length on the structure and phase behaviour of phospholipid–gramicidin bilayers,” Phys Chem Chem Phys, vol. 2, pp. 4545–51, 2000.
[41] W.S.L. Mok and M.J. Antal, “Uncatalyzedsolvolysis of whole biomass hemicellulose by hot compressed liquid water,” Ind. Eng. Chem. Res., vol. 31, no. 4, pp. 1157–1161, Apr. 1992.
[42] G. Garrote, H. Domínguez, and J. C. Parajó, “Hydrothermal processing of lignocellulosic materials,” HolzalsRoh- und Werkstoff, vol. 57, no. 3, pp. 191–202, Jun. 1999.
[43] M. Déniel, G. Haarlemmer, A. Roubaud, E. Weiss-Hortala, and J. Fages, “Hydrothermal liquefaction of blackcurrant pomace and model molecules: understanding of reaction mechanisms,” Sustainable Energy Fuels, vol. 1, no. 3, pp. 555–582, May 2017.
[44] Y. Gao, H. Chen, J. Wang, T. Shi, H.P. Yang, and X.H. Wang, “Characterization of products from hydrothermal liquefaction and carbonation of biomass model compounds and real biomass,” Journal of Fuel Chemistry and Technology, vol. 39, no. 12, pp. 893–900, Dec. 2011.
[45] T.H. Pedersen and L.A. Rosendahl, “Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems,” Biomass and Bioenergy, vol. 83, pp. 206–215, Dec. 2015.
[46] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, “Dissolution and Hydrolysis of Cellulose in Subcritical and Supercritical Water,” Ind Eng Chem Res, vol.39, pp. 2883-2890, 2000.
[47] F. Li, Z. Hu and B. Xiao, “Bio-oil Production by Thermochemical Catalytic Liquefaction of Bloom-Forming Cyanobacteria: Optimization Using Response Surface Methodology (RSM),” Energy Fuels, vol. 31, no. 12, pp. 13733–13742, Dec. 2017.
[48] U. Jena, A.T McCurdy, A. Warren, H. Summers, R.N Ledbetter, S.K. Hoekman, L.C. Seefeldt and C. Jason, “Oleaginous yeast platform for producing biofuels via co-solvent hydrothermal Liquefaction,” Biotechnol Biofuels, vol. 8, pp. 167, 2015.
[49] J.R. Martin, R. Kornsulle, “Process for the extraction of macromolecules from biomass using the stillage,” US Patent, September. 2011.
[50] J. Zhang, Y. Zhang, and Z. Luo, “Hydrothermal Liquefaction of Chlorella Pyrenoidosa in Ethanol-water for Bio-crude Production,” Energy Procedia, vol. 61, pp. 1961–1964, Jan. 2014.
[51] Y.T. Shah,“Energy and fuel systems integration Raton,” Florida: Taylor and Francis Group, 2015.
[52] G. Yu, Y. Zhang, L. Schideman, T. Funk, and Z. Wang, “Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae,” Energy Environ. Sci., vol. 4, no. 11, pp. 4587–4595, Oct. 2011.
[53] D.C. Elliott, L.J. Sealock, M.R. Phelps, G.G. Neuenschwander and T.R. Hart, “Development of a catalytic system for gasification of wet biomass,” NASA STI/Recon Technical Report N, vol. 94, Aug. 1993.
[54] P. Duan and P.E. Savage, “Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts,” Ind. Eng. Chem. Res., vol. 50, no. 1, pp. 52–61, Jan. 2011.
[55] U. Jena, N. Vaidyanathan, S. Chinnasamy, and K. C. Das, “Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass,”

Bioresource Technology, vol. 102, no. 3, pp. 3380–3387, Feb. 2011.
[56] Z. Shuping, W. Yulong, Y. Mingde, I. Kaleem, L. Chun, and J. Tong, "Production and characterization of bio-oil from hydrothermal liquefaction of microalgae Dunaliellatertiolecta cake," Energy, vol. 35, no. 12, pp. 5406–5411, Dec. 2010.
[57] P. Biller and A.B. Ross, "Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content," Bioresource Technology, vol. 102, no. 1, pp. 215–225, Jan. 2011.
[58] U. Jena, K.C. Das, and J.R. Kastner, "Comparison of the effects of Na2CO3, Ca3(PO4)2, and NiO catalysts on the thermochemical liquefaction of microalga Spirulinaplatensis," Applied Energy, vol. 98, pp. 368–375, Oct. 2012.
[59] K. Anastasakis and A.B. Ross, "Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods," Fuel, vol. 139, pp. 546–553, Jan. 2015.
[60] Y.F. Yang, C.P. Feng, Y. Inamori and T. Maekawa, "Analysis of energy conversion characteristics in liquefaction of algae," Resources, Conservation and Recycling, vol. 43, no. 1, pp. 21–33, Dec. 2004.
[61] X.Z. Yuan, J.Y. Tong, G.M. Zeng, H. Li, W. Xie, "Comparative studies of products obtained at different temperatures during straw liquefaction by hot compressed water," Energy Fuels, vol. 10 pp. 3262–7, 2009.
[62] P.J. Valdez, J.G. Dickinson and P.E. Savage, "Characterization of Product Fractions from Hydrothermal Liquefaction of Nannochloropsis sp. and the Influence of Solvents," Energy Fuels, vol. 25, no. 7, pp. 3235–3243, Jul. 2011.
[63] U. Jena and K. C. Das, "Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae," Energy Fuels, vol. 25, no. 11, pp. 5472–5482, Nov. 2011.
[64] C. Yang, L. Jia, C. Chen, G. Liu, and W. Fang, "Bio-oil from hydro-liquefaction of Dunaliellasalina over Ni/REHY catalyst," Bioresource Technology, vol. 102, no. 6, pp. 4580–4584, Mar. 2011.
[65] J. Yang, Q. (Sophia) He, H. Niu, K. Corscadden and T. Astatkie, "Hydrothermal liquefaction of biomass model components for product yield prediction and reaction pathways exploration," Applied Energy, vol. 228, pp. 1618–1628, Oct. 2018.
[66] M. Déniel, G. Haarlemmer, A. Roubaud, E. Weiss-Hortala, and J. Fages, "Modelling and Predictive Study of Hydrothermal Liquefaction: Application to Food Processing Residues," Waste Biomass Valor, vol. 8, no. 6, pp. 2087–2107, Sep. 2017.
[67] D.C. Hietala, C.K. Koss, A. Narwani, A.R. Lashaway, C.M. Godwin, B.J. Cardinale, P.E. Savage, "Influence of biodiversity, biochemical composition, and species identity on the quality of biomass and biocrude oil produced via hydrothermal liquefaction," Algal Research, vol. 26, pp. 203–214, Sep. 2017.
[68] W. Song, S. Wang, Y. Guo and D. Xu, "Bio-oil production from hydrothermal liquefaction of waste Cyanophyta biomass: Influence of process variables and their interactions on the product distributions," International Journal of Hydrogen Energy, vol. 42, no. 31, pp. 20361–20374, Aug. 2017.
[69] J.D. Sheehan and P.E. Savage, "Modeling the effects of microalga biochemical content on the kinetics and biocrude yields from hydrothermal liquefaction," Bioresour. Technol., vol. 239, pp. 144–150, Sep. 2017.
[70] R. Alenezi, G.A. Leeke, R.C.D. Santos and A. R. Khan, "Hydrolysis kinetics of sunflower oil under subcritical water conditions," Chemical Engineering Research and Design, vol. 87, no. 6, pp. 867–873, Jun. 2009.
[71] M.A. Meetani, O.K. Zahid and J.M. Conlon, "Investigation of the pyrolysis products of methionine-enkephalin-Arg-Gly-Leu using liquid chromatography-tandem mass spectrometry," J Mass Spectrom, vol. 45, no. 11, pp. 1320–1331, Nov. 2010.
[72] J.W. King, R.L. Holliday and G. R. List, "Hydrolysis of soybean oil. in a subcritical water flow reactor," Green Chem., vol. 1, no. 6, pp. 261–264, Jan. 1999.
[73] H.Y. Shin, J.H. Ryu, S.Y. Park, and S.Y. Bae, "Thermal stability of fatty acids in subcritical water," Journal of Analytical and Applied Pyrolysis, vol. 98, pp. 250–253, Nov. 2012.
[74] S. Yin and Z. Tan, "Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions," Applied Energy, vol. 92, pp. 234–239, Apr. 2012.
[75] T.M. Aida, N. Shiraishi, M. Kubo, M. Watanabe and R.L. Smith, "Reaction kinetics of d-xylose in sub- and supercritical water," The Journal of Supercritical Fluids, vol. 55, no. 1, pp. 208–216, Nov. 2010.
[76] M. Wahyudiono, Sasaki and M. Goto, "Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water," Chemical Engineering and Processing: Process Intensification, vol. 47, no. 9, pp. 1609–1619, Sep. 2008.
[77] X. Wu, J. Liang, Y. Wu, H. Hu, S. Huang and K. Wu, "Co-liquefaction of microalgae and polypropylene in sub-/super-critical water," RSC Adv., vol. 7, no. 23, pp. 13768–13776, Feb. 2017.
[78] D.A. Cantero, M.D. Bermejo and M.J. Cocero, "Kinetic analysis of cellulose depolymerization reactions in near critical water," The Journal of Supercritical Fluids, vol. 75, pp. 48–57, Mar. 2013.
[79] A. Croce, E. Battistel, S. Chiaberge, S. Spera, F. De Angelis and S. Reale, "A Model Study to Unravel the Complexity of Bio-Oil from Organic Wastes," ChemSusChem, vol. 10, no. 1, pp. 171–181, 2017.
[80] S. Chiaberge, I. Leonardis, T. Fiorani, G. Bianchi, P. Cesti, A. Bosetti, M. Crucianelli, S. Reale and

F.D. Angelis, “Amides in Bio-oil by Hydrothermal Liquefaction of Organic Wastes: A Mass Spectrometric Study of the Thermochemical Reaction Products of Binary Mixtures of Amino Acids and Fatty Acids,” Energy Fuels, vol. 27, no. 9, pp. 5287–5297, Sep. 2013.

[81] T.H. Pedersen, I. Grigoras, J. Hoffmann, S. Toor, I.M. Sintamarean, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Sogaard, L. Rosendahl, “Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation,” Applied Energy, vol. 162, no. C, pp. 1034–1041, 2016.

[82] J. M. Bouvier, M. Gelus and S. Maugendre, “Wood liquefaction-An overview,” Applied Energy, vol. 30, no. 2, pp. 85–98, Jan. 1988.

[83] W. Costanzo, R. Hilten, U. Jena, K. C. Das, and J. R. Kastner, “Effect of low temperature hydrothermal liquefaction on catalytic hydrodenitrogenation of algae biocrude and model macromolecules,” Algal Research, vol. 13, pp. 53–68, Jan. 2016.

[84] Y. Alhassan, N. Kumar and I. M. Bugaje, “Hydrothermal liquefaction of de-oiled Jatrophacurcas cake using Deep Eutectic Solvents (DESs) as catalysts and co-solvents,” Bioresource Technology, vol. 199, pp. 375–381, Jan. 2016.

[85] Z. Zhu, S.S. Toor, L. Rosendahl, D. Yu and G. Chen, “Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw,” Energy, vol. 80, pp. 284–292, Feb. 2015.

[86] J. Zhang, Y. Zhang, Z. Luo, “ Hydrothermal liquefaction of chlorella pyrenoidosa in ethanol-water for bio-crude production,” Energy Procedia, vol. 61, pp. 1961-1964, 2014.

[87] Y. Xu, X. Zheng, H. Yu and X. Hu, “Hydrothermal liquefaction of Chlorella pyrenoidosa for bio-oil production over Ce/HZSM-5,” Bioresource Technology, vol. 156, pp. 1–5, Mar. 2014.

[88] B.E.O. Eboibi, D.M. Lewis, P.J. Ashman and S. Chinnasamy, “Hydrothermal liquefaction of microalgae for biocrude production: Improving the biocrude properties with vacuum distillation,” Bioresource Technology, vol. 174, pp. 212–221, Dec. 2014.

[89] P.T. Patil, U. Armbruster and A. Martin, “Hydrothermal liquefaction of wheat straw in hot compressed water and subcritical water–alcohol mixtures,” The Journal of Supercritical Fluids, vol. 93, pp. 121–129, Sep. 2014.

[90] H.K. Reddy, T. Muppaneni, S. Ponnusamy, N. Sudasinghe, A. Pegallapati, T. Selvaratnam, M. Seger, B. Dungan, N. Nirmalakhandan, T. Schaub, F.M. Holguin, P. Lammers, W. Voorhies, S. Deng, “Temperature effect on hydrothermal liquefaction of Nannochloropsisgaditana and Chlorella sp.,” Applied Energy, vol. 165, pp. 943–951, Mar. 2016.

[91] R. Shakya, J. Whelen, S. Adhikari, R. Mahadevan and S. Neupane, “Effect of temperature and Na_2CO_3 catalyst on hydrothermal liquefaction of algae,” Algal Research, vol. 12, pp. 80–90, Nov. 2015.

[92] K. Tekin, S. Karagöz and S. Bektaş, “Hydrothermal liquefaction of beech wood using a natural calcium borate mineral,” The Journal of Supercritical Fluids, vol. 72, pp. 134–139, Dec. 2012.

[93] Q.V. Bach, M. V. Sillero, K.Q. Tran and J. Skjermo, “Fast hydrothermal liquefaction of a Norwegian macro-alga: Screening tests,” Algal Research, vol. 6, pp. 271–276, Oct. 2014.

[94] A. Plis, J. Lasek, A. Skawińska, J. Zuwała, “Thermochemical and kinetic analysis of the pyrolysis process in Cladophoraglomerata algae,” J Anal Appl Pyrolysis, vol. 115, pp. 166–74, 2015.

[95] M.R. Díaz Rey, M. Cortes-Reyes, C. Herrera, M.A. Larrubia, N. Amadeo, M. Laborde, L.J. Alemany, “Hydrogen-rich gas production from algae-biomass by low temperature catalytic gasification,” Catalysis Today, vol. 257, pp. 177–184, Nov. 2015.

[96] M.A. Sharara, N. Holeman, S.S. Sadaka and T. A. Costello, “Pyrolysis kinetics of algal consortia grown using swine manure wastewater,” Bioresource Technology, vol. 169, pp. 658–666, Oct. 2014.

[97] M.M. Phukan, R.S. Chutia, B.K. Konwar, R. Kataki, “Microalgae Chlorella as a potential bio-energy feedstock,” Appl Energy, vol. 88, pp. 3307–3312, 2011.

[98] M. Ertaş and M. Hakkı Alma, “Pyrolysis of laurel (Laurusnobilis L.) extraction residues in a fixed-bed reactor: Characterization of bio-oil and bio-char,” Journal of Analytical and Applied Pyrolysis, vol. 88, no. 1, pp. 22–29, May 2010.

[99] D. López Barreiro, S. Riede, U. Hornung, A. Kruse and W. Prins, “Hydrothermal liquefaction of microalgae: Effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil,” Algal Research, vol. 12, pp. 206–212, Nov. 2015.

[100] N. Neveux, A.K.L. Yuen, C. Jazrawi, M. Magnusson, B.S. Haynes, A.F. Masters, A. Montoya, N. Paul, T. Maschmeyer, R.D. Nys, “Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae,” Bioresource Technology, vol. 155, pp. 334–341, Mar. 2014.