

EFFECT OF PROCESS CONDITIONS ON HYDROTHERMAL LIQUEFACTION OF BIOMASS

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ABSTRACT: Hydrothermal liquefaction (HTL) is an important thermochemical conversion technique which is generally used to convert biomass into bio-fuels and valuable products. It involves direct liquefaction of biomass, in the presence of water and catalyst, at a temperature of 250-400°C, pressure of 5-25 MPa and residence time of 0-60 min. Various process parameters including liquefaction temperature, residence time, rate of biomass heating, size of biomass particles, and type of solvent affect the yield of bio-oil and quality of the products. So the main objective of this review is to assess the effect of various liquefaction parameters on bio-oil yield. The review concludes with a brief discussion on the opportunities within the field of hydrothermal valorisation of biomass.

Keywords: Biomass, Hydrothermal Liquefaction, Bio-oil, Temperature, Solvent.

1. INTRODUCTION

Increase in world population, industrialization, urbanization, technological advancement, transportation, and high standard of living caused rise in energy demand due to which depletion of fossil fuels takes place. The excess use of fossil fuels as the main energy carrier has resulted in an exponential increase in the atmospheric concentration of greenhouse gases. As a result, several uncertainties like climate change, global warming, increase in CO₂ level and temperature threaten the future of the planet. Depletion, shortage, and uneconomic extraction of fossil fuels have generated an overwhelming interest in exploring alternate sources of energy. So many governments across the globe have turned their policies towards the development of alternative, sustainable and renewable energy sources. Biomass based fuels, if substituted for fossil fuels, have the capability to reduce global warming caused by increased atmospheric concentration of CO₂. Bio-fuels play an increasing role to reduce CO₂ emissions since CO₂ can be fixed by photosynthesis during biomass growth [1]. Biomass is a traditional source of energy and is still responsible for around 40-50% of the energy supply in many developing countries that rely on low-tech and inefficient cooking and heating

methods [2]. It is widely accepted that utilizing biomass as energy source would bring forth social and economical benefits in less developed regions of the world. The conversion of biomass resources has emerged as an attractive alternative to the production of liquid transportation fuels comparable with petroleum.

Biomass is the world's fourth largest energy source worldwide, following coal, oil and natural gas. Generally biomass includes wood, grass, trees, mill scrap, nutshells, switchgrass, sawdust, wood chip, rice straw, rice husk, aquatic species, cattle manure, bagasse, barley straw, sewage sludge, food waste, biological waste etc. [3]. Biomass is a carbon neutral, sustainable, clean, and renewable energy of source. In the future, the lignocellulosic remains of plants, such as agricultural and forestry waste (wood, bark etc.) should be used for energy purpose as these are not in direct competition with biomass for food and feed. Biomass is considered to be a feasible energy resource, since it is abundantly available, renewable, excels at low CO₂ emissions, and exchanges the burden of disposal with benefit of recycling. Biomass processing to produce bio-fuels is of a growing interest and could be economically viable in the future [4].

1.1. Components of biomass

Biomass is a complex mixture of organic materials such as carbohydrates, fats, and proteins, along with small amounts of minerals such as sodium, phosphorus, calcium, iron and their content varies as per species. Fig. 1 shows the major components of biomass. Main constituents of biomass are cellulose, hemicellulose, and lignin.

Cellulose is primarily composed of d-glucose, which is made of six carbons or hexose sugars [3]. Cellulose has a high degree of crystallinity, which renders it insoluble in water and resistant to attack by enzymes. However, at subcritical conditions cellulose is rapidly solubilised and hydrolyzed to its constituents. Hemicelluloses are a chain of sugars, containing arabinose, galactose, glucose, mannose and xylose [5]. Hemicellulose degrades easily as heat treatment is applied on it as it is more unstable as compared to cellulose. Due to its non-crystalline nature, hemicellulose is more susceptible to depolymerisation than cellulose.

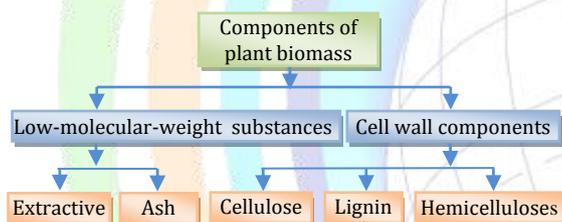


Fig. 1 Major components in biomass

Lignin is an amorphous and heterogeneous substance, containing phenol-propane backbone. Lignin is hydrophobic in nature as its solubility is very low in water. Woody plants have more lignin as compared to herbaceous plant because in woody plants fibres are tightly bonded. Lignin can be a promising source for chemicals, such as phenols and aromatics. Lignin is a complex network polymer of three main lignin building blocks, i.e., p-hydroxy-phenyl-propanol, guaiacyl-propanol, and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and β -1 linkages) and ether linkages (e.g., β -O-4 and R-O-4), with the ether linkages being the dominant linkages between the three main lignin building blocks [6]. Table 1 depicts the major products obtained from constituents of

biomass [7]. Lignin has higher energy content and it provides a biomass with a higher heating value [8].

Table 1: Major products of Cellulose, Hemicellulose, and Lignin

Cellulose	Glucose, Fructose, Erythrose, 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA), Lactic acid, Acetic acid, Aldehydes, Alcohols, Phenols etc.
Hemicellulose	Xylose, Arabinose, Mannose, Fructose, Glucose, Erythrose, Dihydroxyacetone, Furfurals, Acetic acid, Formic acid etc.
Lignin	Syringols, Guaiacols, Catechols, Acids, Aldehydes, Alcohols, Phenol and its derivatives etc.

It provides waterproofing, structural reinforcement, and resilience to biological and physical attack compared to all-carbohydrate cell walls of immature plant tissues. Lignin serves as a sort of glue giving the biomass fibres its structural strength, while cellulose and hemicellulose polymers are the basic building blocks of fibres. Extractives are composed of a wide range of organic and inorganic compounds like proteins, fats, sugars, fatty acids, phenols, and resin. They are classified on the basis of solvent used to extract them i.e., water soluble, toluene-ether soluble or ether soluble [9].

2. ENERGY FROM BIOMASS

Biomass consists of a variety of materials with distinctive physical and chemical characteristics. Conversion of lignocellulosic biomass to bio-fuels offers major economic, environmental, and strategic benefits. It may be converted to energy by different processes, depending on the raw characteristics of the material and the type of energy desired. Biomass conversion can be divided into two main conversion pathways: Biochemical and thermochemical conversion [1] as shown in Fig. 2.

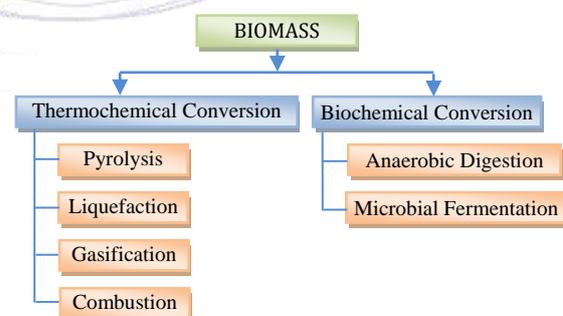


Fig. 2 Biomass conversion pathways

2.1. Biochemical Process

Biochemical conversion of biomass is completed through alcoholic fermentation to produce liquid fuels and anaerobic digestion or fermentation to produce bio-gas [10]. In fermentation process conversion of sugar into ethanol in the presence of yeasts takes places, whereas anaerobic process organic matter converts into gaseous products by using bacteria. Degradation of woody biomass into sugars is a difficult and expensive process.

2.2. Thermochemical Process

Thermochemical conversion includes gasification, hydrothermal liquefaction and pyrolysis [11]. Biomass is converted into synthesis gas through gasification or bio-oils through pyrolysis and hydrothermal liquefaction (HTL), which can be further upgraded to liquid fuels (e.g., gasoline and diesel fuel) and other valuable chemicals. In gasification process, oxidation of biomass occurs by using gasification agents i.e., air and steam. Main product of gasification process is producer gas. Pyrolysis is a thermal decomposition process operating at atmospheric pressure in absence of oxygen to produce bio-oil, charcoal, and gas. Liquefaction includes cracking of biomass molecules at low temperature and high pressure. The main advantage of liquefaction process is low temperature requirement.

3. HTL PROCESS

Hydrothermal liquefaction (HTL) process converts biomass into liquid products with high energy content in the presence of water at temperature less than 400°C. Under these conditions water obtains a set of unique properties that facilitates depolymerisation, hydrolysis, and decomposition of biomass to produce a water insoluble bio-oil. HTL process is also known as Hydrous Pyrolysis. This process is very robust in the sense that it accepts many types of biomass, such as algae, wood or even waste biomass like municipal waste, industrial by-products or manure [12].

In tropical grasses, water content is more than 80-85% or ~ 90% for aquatic species, while

pyrolytic liquefaction liquefies biomass having < 40% of moisture content. Drying of sample is the best outcome for this problem. Solar drying is generally used, but it takes longer time to lower the moisture content of biomass. Thus, HTL is a best method and offers high energy efficiency, where water is used as good solvent and act as catalyst for the degradation of organic compounds.

The difference between oil from HTL process and fossil fuel process is that in fossil fuels more time is required to obtain the liquid fuels than HTL process. In HTL process the requirement of time is hours and minutes where as in fossil fuels it takes many years. Wet biomass, containing more than 50 % wt of water, is unattractive feedstock for further utilization due to increased transport costs, and environmental considerations related to unpleasant odour, large number of pathogens including bacteria, viruses and parasites. The schematic representation of HTL process is depicted in Fig. 3. HTL technologies also have the potential for producing a range of chemicals including vanillin, phenols, aldehydes, and acetic acids. The advantages of HTL process are its applicability for high-moisture-content biomass, use of lower temperatures, and high energy efficiency [13]. For this reason, HTL process gains much attention during last decades as very perspective conversion routes for wet biomass waste, especially for these of very high water content. In this review paper, the effects of the biomass composition and structure, reaction temperature, residence time, heating rate, and pressure during hydrothermal liquefaction on the overall yield of the volatiles are discussed.

Recent developments of HTL technology include efficient liquefaction of various biomass in near-/super-critical water and organic solvents with a suitable catalyst obtaining a total liquid yield of 40-60 wt%. The detailed classification, operating conditions, and reaction pathways for HTL processes of biomass were extensively summarized in the literatures. Hydrothermal liquefaction (HTL) is a promising second-generation method for production of energy from biomass waste.

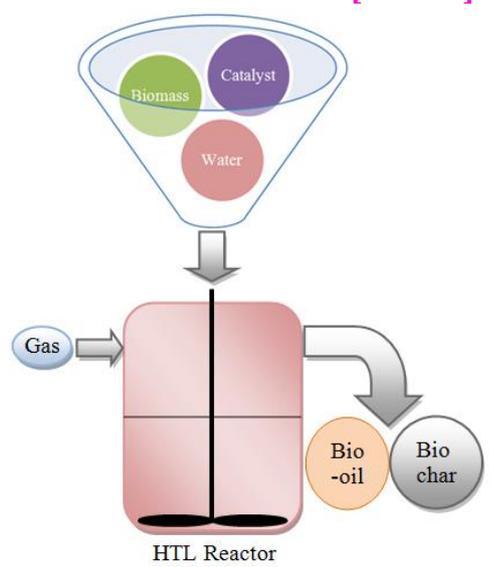


Fig. 3 Schematic diagram of HTL process

3.1. Role of water in HTL Process

The unique properties of water at high temperature and high pressure play a significant role in subcritical hydrothermal liquefaction of biomass to bio-oil. Water is safe, non-toxic, readily available, inexpensive, and environmentally benign solvent [14]. At normal conditions water will not react with organic compounds. The properties of water change with increase in temperature. Moreover, water itself has a catalytic role in various acid/base catalysed processes due to its higher degree of ionization at the increased temperature. Under the HTL conditions water is a powerful polar organic solvent due to the strong decrease of its dielectric constant with temperature. Water molecules isolate the reaction intermediates and serve as a physical barrier between them. In fact, water is the driving force in HTL, as it acts both as a reactant and a catalyst. High diffusivity, low viscosity and high miscibility can speed up reactions and improves its reaction efficiency [15].

4. EFFECTS of PROCESSING PARAMETERS

The processing parameters of HTL include reaction temperature, retention time, biomass loading, pressure, reducing gas, hydrogen donor solvent, in which reaction temperature and

retention time have significant effects on biomass HTL. Their effects on bio-oil yield and quality is discussed below.

4.1. Effect of Temperature

Temperature is the most important parameter of HTL process. Many researchers have studied the influence of temperature on HTL of biomass to bio-oil [16-33]. The reaction temperature higher than 374°C leads to formation of gases [16]. Bio-oil formation from lignocellulosic biomass mainly occurred at the temperature range of 200 to 400°C, in which bio-oil yield increased with increasing reaction temperature, and then decreased as temperature increased further [19-22]. Fig. 4 provides information about the relationship between the temperature and bio-oil yield and the studies summarized only serve as a qualitative comparison due to the use of different biomass feedstocks, residence times, pressure, gas, and methods of analysis. Liquefaction of biomass at low temperature generally produced insignificant amount of liquid oils. Karagoz et al., 2004 [24] investigated the liquefaction of sawdust at different temperatures 180°C, 250°C, and 280°C. The total bio-oil yield at these temperatures was found to be 3.7 wt.%, 7.6 wt.% and 8.5 wt.% respectively. Liu et al., 2012 [30] observed that highest conversion and yield of bio-oil (32.7 wt. %) for liquefaction of cypress was observed at a reaction temperature of 260°C. Tekin et al., 2012 [31] reported the effects of operating parameters on the hydrothermal liquefaction of beech wood at different temperatures 250, 300, and 350°C with and without colemanite. The highest light bio-oil yield (11.1 wt.%), and highest heavy bio-oil yield (29.8 wt.%) were obtained at 300°C with colemanite. Wang et al., 2013 [32] observed that temperature range of 300-315°C was suitable for efficient production of liquid oils. Liu et al., 2014 [33] reported that bio-oil yield and conversion of sawdust increased continuously with increase in temperature. The most suitable temperature for hydrothermal liquefaction was found to be 300°C. However, for some biomasses high temperature may be required.

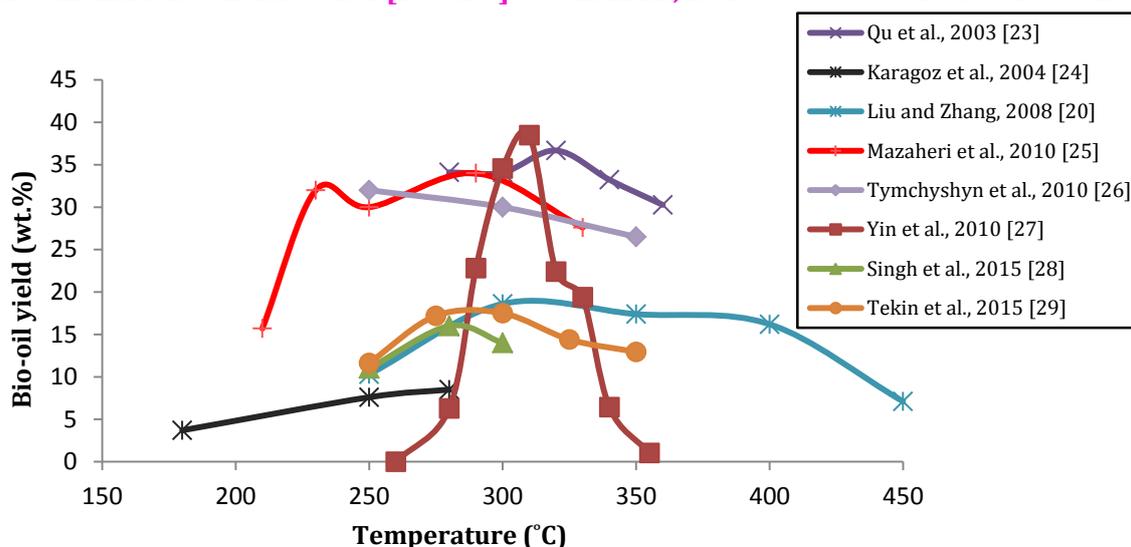


Fig. 4 Effect of reaction temperature on bio-oil yield

4.2. Particle Size

For hydrothermal liquefaction process particle size is generally considered as a secondary parameter as it imparts no significant impact on the yield of bio-oil. In hydrothermal liquefaction process particle size of 4-10 mm is preferred. Particle size increases the utility of biomass by which higher degree of fragmentation and hydrolysis takes place. So more bio-oil yield will be obtained with more degree of hydrolysis and fragmentation. But cost of process increases with reduction in particle size. Grinding cost became double for wheat straw, barley straw, and switch grass as more energy is utilized to convert coarse particles to fine particles [34]. Zhang et al., 2009 [35] investigated HTL of grass perennials with three different particle sizes and concluded that reduction in particle size did not increase the bio-oil yield at temperature of 350°C.

4.3. Effect of Biomass Feedstock

Biomass is composed of cellulose, hemicellulose and lignin and varies as per biomass feedstock. Differences in the composition cause heterogeneity by which bio-oil yield also differs. The chemical

structure of lignin is more complex than cellulose and hemicelluloses. The degradation temperature of lignin is more as compared to cellulose and hemicellulose. Generally cellulose and hemicellulose enhance the liquid bio-oil yield whereas lignin imparts negative effect on bio-oil yield. Lignin is difficult to be converted into bio-oil at neutral conditions due to its thermal stability and complex structure. Lignin has a higher degree of polymerization and complex branching, so it is decomposed relatively at higher temperature. Lignin is physically and chemically stable until high temperatures above 350°C [36]. So lignin produces low oil fractions during HTL process. Hence cellulose rather than lignin in lignocellulosic biomass dominates bio-oil production at neutral conditions.

There is a strong positive relationship between lignin content and bio-oil yield at alkaline conditions. Bhasker et al., 2008 [37] found that cherry with higher lignin content produced more bio-oil than cypress with lower lignin content at 280°C with alkali catalyst. Physical properties of lignin result in bio-oil with high oxygen and moisture content, thus lowering oil quality and HHV. The major reason for variation in

bio-oil composition is due to variations in biomass feedstock and lignocellulosic components present in it. Table 2 shows the chemical composition of various feedstocks.

Table 2: Chemical composition of various biomass feedstocks (wt.%)

Feed	Cellulose	Hemicellulose	Lignin	Ref.
Wheat straw	45.20	33.82	20.98	[38]
Corn cob	32.32	52.49	17.48	[38]
Spruce wood	21.31	47.11	31.58	[38]
Rice straw	27.2	34.0	14.2	[39]
Birch wood	25.7	40.0	15.7	[39]
Softwood	40-50	20-40	25-35	[40]
Hardwood	40-50	20-40	18-25	[40]
Sawdust	32.63	37.23	22.16	[41]

4.4. Effect of Heating Rate

For HTL process high heating rates are favorable for bulk fragmentation of biomass. The occurrence of secondary reactions at slow heating rate leads to formation of char residue. Secondary reactions also become dominant at very high heating rates, which results in high gas yields. Even heating rates have less effect on HTL as compared to pyrolysis process. This is because hot compressed water is used for better dissolution and for stabilization of fragmented species. Zhang et al., 2009 [35] found that increasing the heating rate from 5 to 140°C min⁻¹ reduced ash and gas yields from 19.8 to 8.9% and 28.7 to 20.5%, respectively. Generally moderate heating rates are preferable to overcome heat and produce high liquid-oil compounds.

4.5. Effect of Solvent Density

The important parameter is biomass to water ratio. Effect of water and solvent density on hydrothermal liquefaction was observed by different researchers. The use of solvent generally enhances the stability and solubility of fragmented compounds. Higher amount of water enhanced the yield of liquid and gas [42]. At very low biomass

to solvent ratio, the liquid yield decreases. But it is not economical to use a lot of water, since it requires more energy and more cost for the waste water treatment [23].

4.6. Effect of Pressure

Pressure is one of the main parameters for degradation of biomass. In the two phase system, there is need of large heat supply to maintain the temperature of the system [43]. Pressure helps to maintain single phase media for liquefaction process. The rate of hydrolysis and biomass dissolution can be controlled by maintaining pressure above the critical pressure of biomass. Solvent density increases as pressure increases. Enhanced decomposition and extraction can be achieved as high density medium penetrates properly into molecules of biomass components [44]. As supercritical conditions is achieved, pressure imparts little or negligible influence on the yield of liquid oil or gas yield [45-48]. Yin et al., 2010 [27] investigated the liquefaction of cattle manure to bio-oil and found that CO was the most effective process gas for bio-oil yield. The higher initial pressure of CO decreased bio-oil yield. Sangon et al., 2006 [45] concluded that pressure imparted little or negligible effect on the yield of liquid oil and gas. While the pressure hardly constitutes an important parameter for the overall bio-oil yield, it plays a crucial part in the overall energy consumption of the HTL process.

4.7. Effect of Residence Time

Residence time is an another important parameter in HTL process. So numerous researchers have investigated the effect of residence time on product distribution during HTL process [23, 27-30, 32, 35, 49-53]. The yield of bio-oil as a function of residence time is shown in Fig. 5 and optimal residence time appears confusing just like optimal reaction temperature.

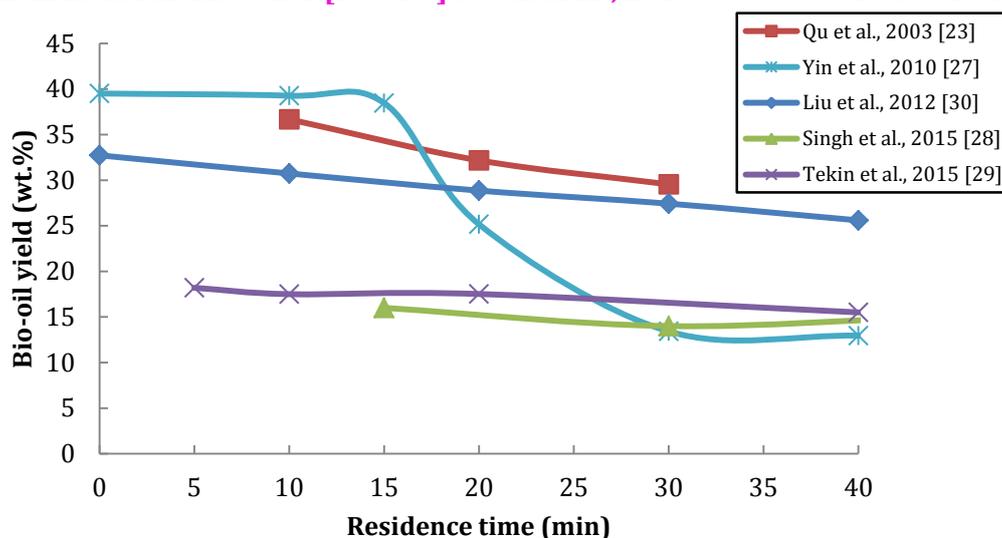


Fig. 5 Effect of residence time on bio-oil yield

However shorter residence time is generally preferred for HTL process. Short residence time at high temperature gives higher yield of oil, while at high temperature higher residence time increases the yield of solid residue. Boocock and Sherman 2009 [51] observed that longer residence times suppressed the bio-oil yield except for very high biomass to water ratios. Zhang et al., 2009 [35] found that extending the duration of the reaction accelerated the gas and char formation due to the occurrence of secondary and tertiary reactions. Similar findings were obtained by Qu et al., 2003 [23] and Karagöz et al., 2004 [41]. Yin et al., 2010 [27] observed that longer residence time decreased the bio-oil yield regardless of the process gas. Jena et al., 2011 [52] and Valdez et al., 2012 [53] found that the increase of reaction time reduced the yield of heavy bio-oil while enhancing the light bio-oil yield. In general, shorter residence time is preferred due to higher bio-oil yield and lower heat loss per unit mass of bio-oil.

4.8. Effect of reducing gas / hydrogen donor solvent

Reducing gases and hydrogen donors are used to stabilize the fragmented products of liquefaction. Generally these act as stabilizers as they inhibit condensation, cyclization and re-polymerization of free radicals. The most effective stabilizing agent is hydrogen, but it is a costly option. Different gases are used as reducing agents like steam, synthesis gas (CO/H₂), N₂ and argon etc. Air leads to the combustion of biomass, due to this it cannot be used as reducing gas. Yin et al., 2010 [27] concluded that reactive gases were better as compared to inert gases in HTL process. H₂ and synthesis gas is recommended to use as reducing gases. Due to hazardous nature of CO, it should not be used as reducing gas. The most popular solvent for hydrogenation of fragmented species is tetralin. Effect of reducing gas and hydrogen donor solvents is shown in table 3. Beauchet et al., 2011 [54] liquefied straw, wood, and sawdust in the presence of tetralin as solvent and it was concluded that use of tetralin as solvent avoided the recondensation of the intermediate products. Reducing gases impart secondary effect on the liquid yield and modify the product composition of liquefaction.

Table 3: Effect of reducing gas/hydrogen donor solvent on bio-oil yield

Biomass Type	Reducing gas/Hydrogen donor Solvents	Bio-oil yield	Concluding Remarks	Ref.
Cellulose	N ₂ , CO, and CO ₂	Bio-oil yield was 31 wt.%, 34 wt.%, and 34 wt.% by using N ₂ , CO, CO ₂ as process gases respectively.	Higher bio-oil yields were produced with H ₂ as process gas than with N ₂ .	Donovan et al.,1981 [55]
Swine Manure	CO, H ₂ , CO ₂ , N ₂ , and compressed air	Oil production efficiency by using CO, N ₂ , CO ₂ , H ₂ , and air was 5.71%, 64.9%, 60.8%, 77.7%, and 70.2% respectively.	Addition of reducing gases yielded a better quality oil product and achieved higher oil production efficiency.	He et al., 2001 [56]
Sawdust	H ₂ , syngas, CO and Ar as gases, Tetralin as solvent	Bio-oil yield with syngas, Ar, CO, and H ₂ was 48.4%, 46.1 %, 47.9%, and 51.6% with tetralin as solvent and was 29.5%, 27.3%, 25.5%, and 31.6% respectively without tetralin solvent.	Hydrogen donor solvent favored the molecular rearrangement, stabilization of free radicals, and hydrocracking of heavier molecules to light ones due to its penetration and hydrogen-supply abilities.	Wang et al., 2007 [57]
Cattle Manure	CO, H ₂ , N ₂ , and Air	Bio-oil yield was 48.76 wt.%, 44.72wt.%, 38.42 wt.%, and 27.97 wt.% by using CO, H ₂ , N ₂ , and air as process gases.	HTL of cattle manure with CO and H ₂ as process gases produced higher bio-oil yields than N ₂ .	Yin et al., 2010 [27]

5. CONCLUSION

Temperature, type of solvent, solvent density and kind of biomass are the main factors that influence the composition and yield of the bio-oil obtained from HTL. The most influencing parameter on bio-yield is temperature. High solvent to biomass ratio is usually not desired because of high cost and waste water treatment problems. Other parameters are residence time, heating rate, particle size of biomass, and reducing gas or hydrogen donor solvents. Change in composition in HTL is due to variation in components of biomass. More lignin present in biomass causes delay in process and char formation, while hemicellulose and cellulose increase the yield of bio-oil. The operating parameters are required to be studied extensively for optimization. More work is needed to identify suitable catalyst for HTL to increase bio-oil yield. More emphasis should be given on the decomposition behavior of biomass and kinetic model. Thus, there is tremendous potential for this field and the outlook is bright.

REFERENCES

1. Demirbas, A. (2001). Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Mgmt*, 42, 1357-1378.
2. Hamelinck, C. N., and Faaij A. P. C. (2006). Outlook for advanced biofuels. *Energy Policy*, 34, 3268-3283.
3. Basu P. Biomass gasification and pyrolysis: Practical design and theory. 1st ed. Oxford: Elsevier; 2010.
4. Grahn, M., Azar, C., Lindgren, K., Berndes, G., and Gielen, D. (2007). Biomass for heat or as transportation fuel? A comparison between two model-based studies. *Biomass and Bioenergy*, 31(11), 747-758.
5. Willför, S., Sundberg, A., Hemming, J., and Holmbom, B. (2005). Polysaccharides in some industrially important softwood species. *Wood Science and Technology*, 39(4), 245-257.
6. Cheng, S., D'cruz, I., Wang, M., Leitch, M., and Xu, C. (2010). Highly Efficient Liquefaction of Woody Biomass in Hot-

- Compressed Alcohol–Water Co-solvents. *Energy and Fuels*, 24(9), 4659-4667.
7. Behrendt, F., Neubauer, Y., Oevermann, M., Wilmes, B., and Zobel, N. (2008). Direct liquefaction of biomass. *Chemical engineering and technology*, 31(5), 667-677.
 8. Vassilev, S. V., Baxter, D., Andersen, L. K., Vassileva, C. G., and Morgan, T. J. (2012). An overview of the organic and inorganic phase composition of biomass. *Fuel*, 94, 1-33.
 9. Rowell, R. M. (Ed.). (2012). *Handbook of wood chemistry and wood composites*. CRC press.
 10. Demirbas, M. F., and Balat, M. (2006). Recent advances on the production and utilization trends of bio-fuels: A global perspective. *Energy Conversion and Management*, 47, 2371-2381.
 11. Demirbas, A. (2007). Products from lignocellulosic materials via degradation processes. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 30(1), 27-37.
 12. Mørup, A. J., Christensen, P. R., Aarup, D. F., Dithmer, L., Mamakhel, A., Glasius, M., and Iversen, B. B. (2012). Hydrothermal liquefaction of dried distillers grains with solubles: a reaction temperature study. *Energy and Fuels*, 26(9), 5944-5953.
 13. Peterson, Andrew A. (2008), et al. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy & Environmental Science* 1, 32-65.
 14. Savage, P. E. (2009). A perspective on catalysis in sub- and supercritical water. *The Journal of Supercritical Fluids*, 47(3), 407-414.
 15. Demirbas, A. (2011). Competitive Liquid biofuels from Biomass. *Applied Energy*, 88, 17-28.
 16. Zhong, C., and Wei, X. (2004). A comparative experimental study on the liquefaction of wood. *Energy*, 29, 1731-41.
 17. Qian, Y., Zuo, C., Tan, J., and He, J. (2007). Structural analysis of bio-oils from sub- and supercritical water liquefaction of woody biomass. *Energy*, 32, 196-202.
 18. Yuan, X. Z., Li, H., Zeng, G. M., Tong, J. Y., and Xie, W. (2007). Sub- and supercritical liquefaction of rice straw in the presence of ethanol-water and 2-propanol-water mixture. *Energy* 32(11), 2081-2088.
 19. Xu, C., and Lad, N. (2008). Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water. *Energy and Fuels*, 22, 635-642.
 20. Liu, Z., and Zhang, F. S. (2008). Effect of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management*, 49(12), 3498-3504.
 21. Xu, C., and Lancaster, J. (2008). Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. *Water Research* 42(6), 1571-1582.
 22. Duan, P., Chang, Z., Xu, Y., Bai, X., Wang, F., and Zhang, L. (2013). Hydrothermal processing of duckweed: Effect of reaction conditions on product distribution and composition. *Bioresource technology*, 135, 710-719.
 23. Qu, Y., Wei, X., and Zhong, C. (2003). Experimental Study on The Direct Liquefaction of *Cunninghamia Lanceolata* in Water. *Energy*, 28, 597-606.
 24. Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., and Uddin, M. A. (2004). Low-temperature hydrothermal treatment of biomass: effect of reaction parameters on products and boiling point distributions. *Energy and Fuels*, 18(1), 234-241.

25. Mazaheri, H., Lee, K. T., Bhatia, S., and Mohamed, A.R. (2010). Subcritical water liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of catalysts. *Bioresource technology*, 101(2), 745-751.
26. Tymchyshyn, M., and Xu, C. C. (2010). Liquefaction of bio-mass in hot-compressed water for the production of phenolic compounds. *Bioresource technology*, 101(7), 2483-2490.
27. Yin, S., Dolan, R., Harris, M., and Tan, Z. (2010). Subcritical hydrothermal liquefaction of cattle manure to bio-oil: Effects of conversion parameters on bio-oil yield and characterization of bio-oil. *Bioresource technology*, 101(10), 3657-3664.
28. Singh, R., Balagurumurthy, B., Prakash, A., and Bhaskar, T. (2015). Catalytic hydrothermal liquefaction of water hyacinth. *Bioresource technology*, 178, 157-165.
29. Tekin, K., Akalin, M. K., and Karagöz, S. (2015). The effects of water tolerant Lewis acids on the hydrothermal liquefaction of lignocellulosic biomass. *Journal of the Energy Institute*. doi:10.1016/j.joei.2015.06.003
30. Liu, H. M., Xie, X. A., Li, M. F., and Sun, R. C. (2012). Hydrothermal liquefaction of cypress: effects of reaction conditions on 5-lump distribution and composition. *Journal of Analytical and Applied Pyrolysis*, 94, 177-183.
31. Tekin, K., Karagöz, S., and Bektaş, S. (2012). Hydrothermal liquefaction of beech wood using a natural calcium borate mineral. *The Journal of Supercritical Fluids*, 72, 134-139.
32. Wang, F., Chang, Z., Duan, P., Yan, W., Xu, Y., Zhang, L., ...& Fan, Y. (2013). Hydrothermal liquefaction of Litsea cubeba seed to produce bio-oils. *Bioresource technology*, 149, 509-515.
33. Liu, D., Song, L., Wu, P., Liu, Y., Li, Q., and Yan, Z. (2014). Direct hydro-liquefaction of sawdust in petroleum ether and comprehensive bio-oil products analysis. *Bioresource technology*, 155, 152-160.
34. Mani, S., Tabil, L. G., and Sokhansanj, S. (2004). Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass and Bioenergy*, 27(4), 339-352.
35. Zhang, B., von Keitz, M., and Valentas, K. (2009). Thermochemical liquefaction of high-diversity grassland perennials. *Journal of Analytical and Applied Pyrolysis*, 84(1), 18-24.
36. Bobleter, O. (1994). Hydrothermal degradation of polymers derived from plants. *Progress in polymer science*, 19(5), 797-841.
37. Bhaskar, T., Sera, A., Muto, A., and Sakata, Y. (2008). Hydrothermal upgrading of wood biomass: influence of the addition of K₂CO₃ and cellulose/lignin ratio. *Fuel*, 87(10), 2236-2242.
38. Demirbaş, A. (2001). Relationships between lignin contents and heating values of biomass. *Energy conversion and management*, 42(2), 183-188.
39. Mohan, D., Pittman, C. U., and Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & Fuels*, 20(3), 848-889.
40. Fengel, A., and Wegener, G. (1983). *Wood: chemistry, ultrastructure, reactions*. Walter de Gruyter & Co.
41. Jindal, M. K., and Jha, M. K. (2015). Catalytic Hydrothermal Liquefaction of Waste Furniture Sawdust to Bio-oil. *Indian Chemical Engineer*, doi:10.1080/00194506.2015.1006145.
42. Demirbas, A. (2004). Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. *Journal of analytical and applied pyrolysis*, 71(2), 803-815.
43. Goudnaan, F., Van de Beld, B., Boerefijn, F. R., Bos, G. M., Naber, J. E., Van der

- Wal, S., and Zeevalkink, J. A. (2008). Thermal efficiency of the HTU@ process for biomass liquefaction. *Progress in thermochemical biomass conversion*, 1312-1325.
44. Deshpande, G., Holder, G., and Shah, Y. (1985). Effect of solvent density on coal-liquefaction under supercritical conditions. In *abstracts of papers of The American Chemical Society* (Vol. 190, Pp. 41-Ful).
45. Sangon, S., Ratanavaraha, S., Ngamprasertsith, S., and Prasassarakich, P. (2006). Coal liquefaction using supercritical toluene-tetralin mixture in a semi-continuous reactor. *Fuel processing technology*, 87(3), 201-207.
46. Kersten, S. R., Potic, B., Prins, W., and Van Swaaij, W. P. (2006). Gasification of model compounds and wood in hot compressed water. *Industrial and engineering chemistry research*, 45(12), 4169-4177.
47. Kabyemela, B. M., Takigawa, M., Adschiri, T., Malaluan, R. M., and Arai, K. (1998). Mechanism and kinetics of cellobiose decomposition in sub-and supercritical water. *Industrial and Engineering Chemistry Research*, 37(2), 357-361.
48. Kabyemela, B. M., Adschiri, T., Malaluan, R. M., and Arai, K. (1997). Kinetics of glucose epimerization and decomposition in subcritical and supercritical water. *Industrial and Engineering Chemistry Research*, 36(5), 1552-1558.
49. Zhang, H F., Su, X. L., Sun, D. K., Zhang, R., and Bi, J. C. (2007). Investigation on degradation of polyethylene to oil in a continuous supercritical water reactor. *Journal of Fuel Chemistry and Technology*, 35(4), 487-491.
50. Yan, Y., Xu, J., Li, T., and Ren, Z. (1999). Liquefaction of sawdust for liquid fuel. *Fuel Processing Technology*, 60(2), 135-143.
51. Boocock, D.G.B., and Sherman, K.M. (2009). Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis. *Can J ChemEng*, 63, 627-33.
52. Jena, U., Das, K. C., and Kastner, J. R. (2011). Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*. *Bioresource technology*, 102(10), 6221-6229.
53. Valdez, P.J., Nelson, M.C., Wang, H.Y., Lin, X.N., and Savage, P.E. (2012). Hydrothermal liquefaction of *Nannochloropsis* sp.: Systematic study of process variables and analysis of the product fractions. *Biomass and Bioenergy*, 46, 317-331.
54. Beauchet, R., Pinard, L., Kpogbemabou, D., Laduranty, J., Lemée, L., Lemberton, J. L., ... and Barbier, J. (2011). Hydroliquefaction of green wastes to produce fuels. *Bioresource technology*, 102(10), 6200-6207.
55. Donovan, J. M., Molton, P. M., and Demmitt, T. F. (1981). Effect of pressure, temperature, pH, and carbon monoxide on oil yields from cellulose liquefaction. *Fuel*, 60(10), 898-902.
56. He, B. J., Zhang, Y., Yin, Y., Funk, T. L., and Riskowski, G. L. (2001). Effects of alternative process gases on the thermochemical conversion process of swine manure, *Trans. ASAE*, 44(6), 1873-1880.
57. Wang, G., Li, W., Li, B., and Chen, H. (2007). Direct liquefaction of sawdust under syngas. *Fuel*, 86(10), 1587-1593.