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Liquefaction of lignocellulosic materials and its applications in wood adhesives—A review

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ABSTRACT

Liquefaction, a useful method of turning whole biomass into liquids, provides advantages for energy and polymers and finds applications in many sectors. This paper reviews the different liquefaction technologies and recent advances in the development of sustainable wood adhesives. Current liquefaction technologies include hydrothermal liquefaction (HTL) and moderate acid-catalyzed liquefaction (MACL). HTL produces bio-oils as primary products, and solid residues and gases as by-products. MACL depends on the solvent types used, which are grouped to polyhydric alcohols and phenols. Bio-polyols from alcohol liquefaction, phenolated biomass from phenol liquefaction and phenolic compounds rich-HTL bio-oils have been used in the production of liquefied biomass-based adhesives, which have shown competitive properties but face challenges for industrial uses. Yet, a better understanding of reaction pathways and optimization of the liquefaction processes is needed.

1. Introduction

Lignocellulosic biomass is composed of cellulose, hemicelluloses, lignin and a small number of other substances. It has multiple methods of conversion, various end-products, and wide application areas (Chen, 2015). It has advantages for producing fuels, chemicals, materials and food. Utilization of sustainable and renewable biomass can help solve the problem of material shortages and reduce concerns around the use of non-renewable fossil fuels.

Thermochemical conversion (TCC) (Fig. 1) provides opportunities for converting biomass into desired products, such as: heat, power, electricity, chemicals, fuels, and other value-added materials. The advantages of using TCC technologies are the diverse availability of lignocellulosic materials and the sustainability of the derived products. Principal TCC techniques include combustion, gasification, pyrolysis, and hydrothermal liquefaction (HTL) (Rackemann et al., 2012; Zhang et al., 2010). Pyrolysis and HTL (sometimes called direct liquefaction) both produce liquids known as 'bio-oil' or 'bio-crude' as primary products. Pyrolysis and HTL are sometimes confused with each other since both operations use a similar basic machenism to break down macromolecules (Demirbaş, 2000b). Pyrolysis heats and breaks down dry biomass at high temperature ranging from 370 to 550 °C with a pressure of 0.1–0.5 MPa, in the absence of oxygen (Dimitriadis and Bezergianni, 2017; Zhang et al., 2010). Liquefaction takes place in solvents and can directly convert whole biomass into liquids. HTL requires a temperature between 200–400 °C and a pressure of 5–20 MPa, and occurs in an aqueous environment where water or organic solvents are employed (Dimitriadis and Bezergianni, 2017). Interest in liquefaction was limited in the early 2000s since the reaction mechanisms and fuel upgrading systems were complicated and expensive (Demirbaş, 2001). However, HTL bio-oils show good heat values that are now increasing the interest towards HTL research (Dimitriadis and Bezergianni, 2017). Since HTL has low oil yields and complex products, MACL has been developed with organic solvents at atmospheric pressure and lower temperature than HTL. It can be used for producing desired chemicals and polymers.

There have been increasing numbers of research work on biomass liquefaction and considerable reviews on HTL concerning its processes, bio-oil production and its upgrading. However, reviews on MACL are scarce. The current review was created to fill this gap by providing a thorough understanding of liquefaction developments including a comparison between HTL and MACL. The recent progress of liquefaction was explored by giving details on reaction mechanisms that have not been fully understood, process parameters, and properties of liquefied products and their applications. Emphasis was given to the application of liquefied biomass in environmentally-friendly wood adhesives, in line with current pressures on the wood industry to produce healthier and more sustainable adhesives (Hemmila et al., 2017).

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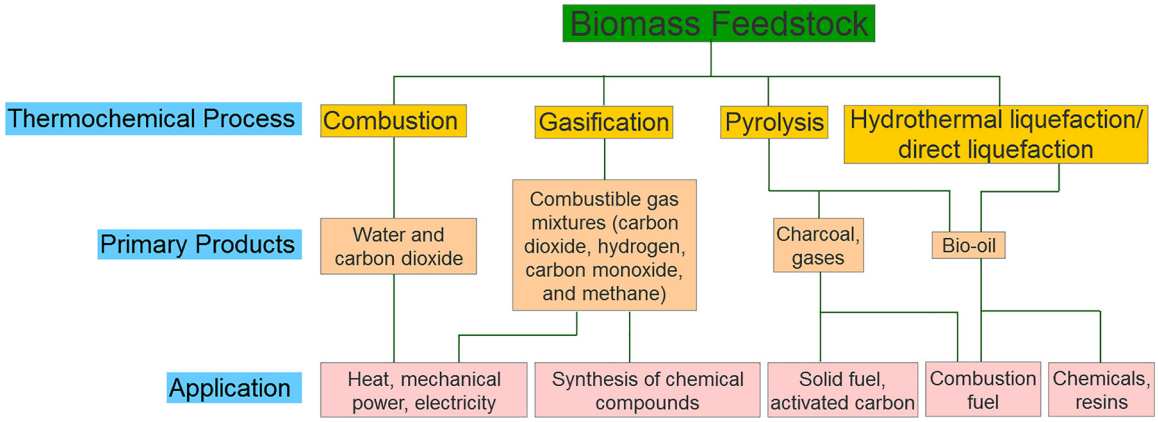

Fig. 1. Primary products and applications from four thermochemical conversions (TCCs) of biomass.

The development of wood adhesives from renewable raw materials has been a topic of considerable interest for many years, which has intensified since the world's oil crisis of the 1970s (Pizzi, 2006). Bio-based adhesives can be derived from natural materials using novel technologies, formulations, and methods. Such adhesives include starch, tannin, lignin, proteins, carbohydrates, rosin, citric acid, unsaturated oils from plants, pyrolysis oil, and liquefied products (Ferdosian et al., 2017; He, 2017; Pizzi, 2006). Bio-based adhesives provide a sustainable solution to formaldehyde concerns in indoor applications, but can also help the wood industry to be less petroleum-dependent (He and Wan, 2017). Previous research on adhesives from liquefied products has shown that the variety of liquefaction derivatives could be compatible not only with formaldehyde-based adhesives for wood panels, but also to other conventional adhesives (e.g. epoxies, polyurethanes, isocyanates) used in the wood industry (Wan et al., 2017). It is important to also note that bio-based adhesives tend to suffer from several issues, which hinder their application at an industrial scale (e.g. availability, lack of adhesion, poor water resistance, viscosity, etc.) (Hemmila et al., 2017). Also, there are currently no economically viable bio-based crosslinkers available on the market, and bio-based adhesives rely on synthetic crosslinkers (typically isocyanates) at a share definitely more than 50% in the final system (e.g. see the commercial thermoplastic starch and soy protein systems). This limitation has also been pointed out for liquefied biomass, so the adhesives derived thereof can not as yet entirely replace the current synthetic resins.

2. Liquefaction of lignocellulosic materials

2.1. Developments and technologies of liquefaction

Biomass liquefaction originates from direct coal liquefaction (DCL), which was commercially started in the 1920s in Germany (Behrendt et al., 2008; Lumpkin, 1988). The biggest advantage of direct liquefaction is the use of the whole coal, peat, and lignocellulosic biomass without a fractionation process (Chornet and Overend, 1985; Hassan and Shukry, 2008). Liquefaction of bio-resources uses wood as the primary source of lignocellulosic biomass (Bouvier et al., 1988). Other biomass such as agricultural crops, energy plants, bio-based wastes (forestry, agricultural, industrial, and life waste) have also been considered for liquefaction. The developments of different liquefaction technologies are illustrated in Table 1.

Hydrothermal liquefaction (HTL) has been developed broadly for converting biomass into bio-oil/bio-crude fuels. It takes place in an aqueous environment where water or organic solvents are employed, with a temperature of 200–400 °C and pressure of 5–20 MPa (Dimitriadis and Bezergianni, 2017). Moderate liquefaction of wood was started in Japan in the 1990s for chemically converting integral wood components into soluble materials and preparing operating plastic films, molding materials, and adhesives (Yamada et al., 2007). Compared with high energy input and costs of HTL, moderate acid catalyzed liquefaction (MACL) develops under low or atmospheric pressure and low temperature at 120–250 °C by using organic solvents (e.g. polyhydric alcohols and phenol) and acid catalysts (Chen, 2015; Hu et al., 2014). Microwave irradiation, ultrasound, and microplasma have been employed in HTL and MACL with the aim of reducing the residence time and improving oil/products yields.

The liquefaction processes can be influenced by either chemical or physical factors. Chemical influencing factors include biomass type and size, solvents and catalysts; physical factors refer to temperature, pressure, solvent to biomass mass ratio, catalyst concentration, heating rate, and residence time (the period during which the maximum temperature is maintained for liquefaction) (Akhtar and Amin, 2011; Behrendt et al., 2008; Dimitriadis and Bezergianni, 2017).

Different lignocellulosic materials including virgin biomass and wastes have been used in liquefaction. Raw biomass materials include agricultural crops, aquatic plants, energy crops, woody plants, and bamboo. Liquefaction is a useful technology for waste management to turn waste (animal, agricultural, forestry, industrial, food) into value-added products. Percentages of cellulose, hemicelluloses, and lignin differ among the biomass types. Table 2 summarizes the chemical composition of different lignocellulosic materials that have been used in the liquefaction. Higher lignin content in the biomass will lead to lower conversion rates and HTL bio-oil yield, as lignin is difficult to degrade and most parts remain in the residues (Akhtar and Amin, 2011; Demirbaş, 2000a,b; Huang and Yuan, 2015). A high ash content also causes low oil yields because of less organic composition and more solid residues left, and inorganic elements in the ash could cover the surface of organic matter and further hamper mass transfer and thermo-chemical reactions between organic matter and solvents (Tian et al., 2014).

Solvents and catalysts play essential roles in the liquefaction process. HTL processes are conducted with or without catalysts, and catalysts are usually used for suppressing tar and char formation (Toor et al., 2011). So far, homogeneous catalysts (such as organic and inorganic acids, alkalis, and salts) are more common and reactive than heterogeneous catalysts. Catalysts that have been studied include acid catalysts (sulfuric acid, oxalic acid, hydrochloric acid, *p*-toluenesulfonic acid), alkalis (sodium hydroxide), metallic salts, and recently acidic ionic acid (Alma et al., 1998a, 1995; Alma et al., 1996a; Janiszewska et al., 2016; Lee and Liu, 2003; Long et al., 2015). It was mentioned by Alma and Shiraishi (1998) that using strong acids for preparing liquefied wood (LW) causes serious corrosion of metallic equipment and environmental pollution compared with alkali catalyst, but promotes more efficient liquefaction. Water, the first liquid solvent employed by liquefaction, shows many shortcomings such as high oxygen content in the derived oils, low oil yields, and also low heating values of the bio-