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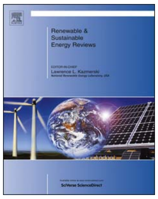

Hydrogen donor solvents in liquefaction of biomass: A review

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ABSTRACT

The environmental impact of global warming, caused by greenhouse gases has also fuelled the needs to utilise biomass, as its energy utilisation creates less environmental pollution and fewer health risks than fossil fuel combustion. Liquefaction of biomass using hydrogen donor solvents is a promising route to obtain clean biofuel using various solvents at moderate to high temperature (250–460 °C) and pressure (150–320 bar). Solvents such as sub-and supercritical water, alcohol, decalin, glycerol and tetralin can be used as potential hydrogen donor to enhance liquid oil yield with a reduced of oxygen content. Supercritical water with its excellent transport properties as well as hydrogen donor capability leads to hydrothermal decomposition of biomass and enhancing various compounds depending upon operating parameters. The selection of alcohol as a solvent related to the action of hydrogen donor and to its alkylating ability. The hydrogen donor solvents provide an alternative to hydrogen gas as a reducing gas. The advantage of using hydrogen donor solvent is to stabilise the free radical in the biomass liquefaction and yielding a higher product conversion. Compared with non-hydrogen donor solvents, hydrogen donor solvents such as tetralin and decalin show significant improvement not only in conversion and product distribution to liquid but also on the quality of bio-oil (oxygen content) due to the improvement of hydrogenation and hydrocracking reactions with inhibition of polycondensation. The advantage of hydrogen donor solvents over the molecular hydrogen due to a lower strength bonding of C-H as compared to H-H bond. A review on performances of water, alcohols and other hydrogen donor solvents in liquefaction of biomass has been made. The yield of hydrogen donated in the reaction has also been reported.

1. Introduction

The biomass energy is produced from wood and wood wastes (64%), followed by municipal solid waste (24%), agricultural waste (5%) and landfill gases (5%) [1]. The utilisation of biomass has become a significant topic recently due to the need to find an alternative to reduce dependency fossil fuels reserves. Fossil fuel resources are finite and non-renewable, catalysing the efforts of employing biomass as a source for the production of renewable energy. Environmental pollution and global energy crisis, caused by the massive use of conventional fossil fuels, have triggered to a move towards sustainable, clean energies and cost-effective energy sources with less pollution and also overcome the gradual depletion of traditional fossil energies [2].

In the production of biomass energy, biochemical and thermochemical conversion are widely employed in a small scale in the laboratory or large scale in the industry [3–7]. Bio-chemical conversion comprises two common processes, digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol) [8]. Thermochemical conversion is the application of thermal to convert the chemical and physical properties of biomass including direct combustion, pyrolysis, gasification, liquefaction and torrefaction. Direct combustion of biomass generates heat and combusted gas of carbon dioxide and water vapor with tar and ash are also produced. However, the major drawbacks are the requirement of high efficiency of combustor due to shapes and form of biomass, as well as the total carbon return to the atmosphere. Liquefaction is a process of producing liquid products in which the feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of suitable catalyst. Meanwhile, gasification is the first step in indirect liquefaction in which the gasifying coal/biomass is partial oxidised to produce syngas, and direct pyrolysis is a conversion process of organic compounds in the inert environment to produce liquid, char and gas products [9,10].

The pyrolysis processes (slow or fast) can be carried out depending on the types of products (liquid, solid or gas) required. Most processes that convert biomass to liquid fuels begin with pyrolysis, followed by

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catalytic upgrading (deoxygenation or hydrotreating) of the resulting biocrude liquids [11]. Deoxygenation (DO) process capable to upgrade oxygenates oil into a higher quality of hydrocarbon based biofuel via decarboxylation/decarbonylation under hydrogen-free atmosphere and produced CO_2/CO as by products. The pyrolysis of various biomass such as beech bark, miscanthus, pine sawdust, sludge, empty fruit bunch, maize, and rice husk have been performed by numerous researchers to produce a liquid yield and chemicals [12–19].

Bio-oil is composed of a complex mixture of oxygenated that provide both the potential and challenge for utilisation. The kinematic viscosity of bio-oil varies from as low as 11 mm^2/s to as high as 115 mm^2/s at 40 °C depending on the nature of the feedstock, temperature of the pyrolysis process, thermal degradation degree and catalytic cracking, the water content of the bio-oil, the amount of light ends that have collected, and the pyrolysis process used [20]. The liquid is highly oxygenated, approximating the elemental composition of the feedstock [21]. The oxygen content of bio-oils is usually 35–40%, distributed in more than 300 compounds depending on the resource of biomass and the severity of the pyrolytic processes [22]. Furthermore, bio-oil with high water content derived from the original moisture in the feedstock will lower the heating value and affect the product quality. Pyrolysis oil is very corrosive as a result of high acidity with average pH values of 2–3 [5]. There are a few methods which can be performed to improve the quality of bio-oil, such as hydrodeoxygenation, catalytic cracking, emulsification and steam reforming.

Hydrothermal liquefaction (HTL), also known as hydrous pyrolysis, is a very flexible technology as far as the type of feedstock is concerned, as a wide variety of bio-based and waste feedstocks have been tested [23]. Bio-oil produced via liquefaction has a reduced oxygen content (10–18%) compared to the parent material (ca. 40%) [24].

Chan et al. reported that bio-oil yields from liquefaction of empty fruit bunch, palm mesocarp fibre and palm kernel shell generally increased when temperature was increased from 330 (sub-critical water) to 390 °C (supercritical water) [25]. The rate of decomposition and cracking of lignocellulosic components from the matrix structure of biomass was enhanced as the temperature was increased, thus leading to increase in formation of bio-oil components. The effects of various solvents, including phenol, ethylene glycol (EG) ethylene carbonate (EC) and supercritical ethanol have been investigated in the liquefaction of biomass [26–29]. Zeb et al. reported that the biomass to solvent ratio (BS) was increased from 0.10 to 0.17 by changing the amount of ethanol, the bio-oil yield decreased significantly from 79.5 to 37.8 wt%, and this was attributed to the combined effect of BS ratio and reaction pressure on the liquefaction reaction [29].

Supercritical fluid extraction is very important to be used in the conversion of biomass. It has been employed to improve bio-oil yield and quality, with much higher calorific values [30]. Durak and Aysu reported that in supercritical liquefaction conditions, acetone was more effective than ethanol and isopropanol in both non-catalytic and catalytic runs at 295 °C with the yields of bio-oil were 21.71% and 25.79% in non-catalytic and catalytic (Ferric chloride) runs respectively [31].

Water has received extensive attention because it is clearly an inexpensive, generates strong hydrogen bonding and high polarity, and easy to recycle reaction medium in liquefaction works [32]. Water can simultaneously act as both a reactant and a catalyst. Hydrothermal liquefaction using subcritical water (200–370 °C and 4–20 MPa) sufficient to keep the water in a liquid state, and going close to the critical point, water has several properties such as low viscosity and high solubility of organic substances, that means it can serve as an excellent medium for fast, homogenous and efficient reactions [33,34]. Both the rate of hydrolysis as well as phase partitioning and solubility of components can be controlled under sub-and supercritical water conditions so that potentially more favourable pathways to gases and liquid biofuels may be realised. The advantage of water in the critical region is still as polar as acetone although the dipole moment decreases with increasing temperature [35].

This review is an effort to elucidate the role of hydrogen donor solvents (alcohols, sub-and supercritical water, tetralin and etc) in liquefaction of biomass, and reporting the product conversion as well as the produced bio-oil yield and also the oxygen content of the produced oil. Some comparison with coal related study also included to give a better insight. The mechanisms of hydrogen donor solvents such as tetralin, cyclohexane and glycerol in liquefaction of biomass have also been discussed and reviewed.

2. Advantages of biomass

Biomass, unlike coal has a relatively high hydrogen-to-carbon ratio. Pure cellulose ($C_6H_{10}O_5$) has a H/C ratio of about 1.7 compared with 0.8 for a typical bituminous coal [36]. The use of biomass can lessen the dependency on the limited fossil fuels and there is the advantage of reduced net carbon dioxide emissions [37–39]. Biomass has the advantage of fixing the carbon dioxide balance in the atmosphere by photosynthesis process. Zero net emission of carbon dioxide (CO_2) can be achieved because CO_2 released from biomass will be reused into the plants by photosynthesis quantitatively [22]. It was reported that by burning large portions of carbon (from fossil fuels) per year we have released (and are continuing to release) enormous quantities of CO_2 within a very short time of about 200 years [40]. CO_2 emissions on g/kW h electricity generation bases are the lowest in the case of biomass (17–27) compared to coal (955), oil (818) and gas (446) [39]. The utilisation of biomass will be beneficial to the environment and society through sustainable energy (renewable biomass), CO_2 neutral fuel, reduction in gases like NOx/SOx due to less sulphur and nitrogen contents present in biomass, and its abundant availability in all regions of the world [41–44]. As such, renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage.

3. Thermochemical conversions

Under the umbrella of thermochemical conversions, biofuels and chemicals can be produced via gasification, pyrolysis and liquefaction. However direct processes (liquefaction and pyrolysis), which have easier methods and are less time consuming, have recently been found to be suitable. The effect of hydrogen donor solvents in liquefaction of biomass will be reviewed in this article.

3.1. Historical background the way towards biomass hydrothermal liquefaction

A number of reports have been published on various aspects of hydrothermal biomass processing over the years. Furthermore, the International Energy Agency conducted the meetings, that bring together researchers and engineers working on thermochemical of biomass conversion, have been held every 3–4 years since 1981; the published proceedings of these conferences offer plenty of information on hydrothermal biomass production [34].

A variety of processes have been researched and patented, initially developed for coal, peat, and wood sludge liquefaction in the 1970's. Early works by Gupta et al. and Chin and Engle in improving the liquid quality have catalysed the research on thermochemical potential as reported by Vasilakos and Austgen [36]. As early as the first oil crisis in the first half of 1970s, direct liquefaction gained attention as one potential pathway from crude oil and was envisaged as a ‘suitable substitute’ for fossil fuels. The difficulties of these early approaches were mainly attributed to the high process prices and the lack of basic scientific understanding of the process, which led to the failure of early works built during that period. However, numerous investigations world-wide led to in a much better understanding of the process. Recent developments and commercialization have targeted waste biomass as a feedstock.