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Review

Hydrothermal liquefaction of agricultural and forestry wastes: state-of-the-art review and future prospects

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ABSTRACT

Hydrothermal liquefaction has been widely applied to obtain bioenergy and high-value chemicals from biomass in the presence of a solvent at moderate to high temperature (200–550 °C) and pressure (5–25 MPa). This article summarizes and discusses the conversion of agricultural and forestry wastes by hydrothermal liquefaction. The history and development of hydrothermal liquefaction technology for lignocellulosic biomass are briefly introduced. The research status in hydrothermal liquefaction of agricultural and forestry wastes is critically reviewed, particularly for the effects of liquefaction conditions on bio-oil yield and the decomposition mechanisms of main components in biomass. The limitations of hydrothermal liquefaction of agricultural and forestry wastes are discussed, and future research priorities are proposed.

1. Introduction

Biomass generally refers to organic substances (except fossil fuels and their derivatives), including plants, animals, microorganisms, as well as organic materials derived from excretion and metabolisms of these organisms, such as agricultural and forestry residues, aquatic plants, urban life, and industrial organic wastes (Duan et al., 2016; Gardner et al., 2015; Hadhoum et al., 2016; Magdeldin et al., 2017; Yu et al., 2017; Zheng et al., 2015). Biomass is the world's fourth most consumed energy source, following the three conventional energy sources, namely, fossil oil, coal, and natural gas. Biomass accounts for 14% of the world's primary energy consumption (Déniel et al., 2016; Haarlemmer et al., 2016). For example, annual output of agricultural straw in China can reach 740 million tons, which is equivalent to 317 million tons of standard coal in calories (Zhang et al., 2016a). Hence, development and utilization of biomass resources can greatly alleviate the depletion of non-renewable fossil fuel.

Compared with fossil energy, biomass energy offers the following advantages (Durak and Aysu, 2016; Doren et al., 2017; Raikova et al., 2016; Yan et al., 2016). (I) Lignocellulosic biomass is renewable because it is derived from plants, which store solar energy. A large number of organisms die every year, and at the same time, numerous new organisms grow. (II) Lignocellulosic biomass is an environmentally friendly energy source, exhibiting low pollution owing to its low sulfur and nitrogen contents, resulting in less generation of SO_x and NO_x during combustion as energy fuel. The amount of carbon dioxide consumed when biomass grows is equivalent to the amount of carbon dioxide released during its production and combustion (Doren et al., 2017; Yan et al., 2016); thus, its growth and combustion process can achieve zero emission of carbon dioxide (Eqs. (1) and (2)). (III) Biomass is universal and easily obtained from the sea and land, including plains and mountains. Therefore, biomass energy development is relatively more popular than other renewable energies, such as solar, wind, geothermal, and tidal energy around the world (Durak and Aysu, 2016).

$$2CO_2 + 5H_2O \xrightarrow{\text{sunlight}} C_6H_{12}O_5 + 6O_2 \quad (1)$$

$$(CH_2O)\ n + nO_2 \longrightarrow nCO_2 + nH_2\ O + \text{Heat energy} \quad (2)$$

Current total biomass estimates are ~400 Gt C based on global aggregation of forest inventories and field observations (Table 1). Human use of biomass products is largely responsible for the difference between actual and potential biomass globally (Pan et al., 2013). As shown in Table 1, tropical forests account for two-thirds of all terrestrial biomass. Temperate and boreal forests are significant, but each source accounts for only ~20% of the tropical biomass. Globally, forests account for 92% of all biomass; therefore, the distribution of forests is tantamount to the distribution of biomass.

Biomass is an efficient and important alternative energy source to

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Table 1
Productivity and total biomass estimates for global terrestrial biomes (Pan et al., 2013).

Biome	Area (10^6 ha)	GPP[a] (Pg C[b] year^{-1})	NPP[c] (Pg C year^{-1})	Current Biomass (Pg C)	Potential Biomass (Pg C)
Tropical forest	1949.4	40.8	21.9	262.1	352.0
Temperate forest	766.7	9.9	8.1	46.6	161.0
Boreal forest	1135.2	8.3	2.6	53.9	180.0
Cropland	1350.0	14.8	4.1	10.8	Not applicable
Other land (except cropland)	7870.0	47.8	25.9	20.0	79.0
Total	13,071.3	121.6	62.6	393.4	772.0

[a] GPP stands for gross primary production.
[b] Pg C stands for petagrams of carbon.
[c] NPP stands for net primary production.

replace fossil fuels in view of the huge amount of agricultural and forestry biomass generated annually around the world. For instance, a joint study by the US Department of Energy and the US Department of Agriculture, often referred to as the "Billion Ton Study", found that roughly 700 million dry tons of non-grain biomass feedstocks could be produced on a renewable basis in the US each year and dedicated to biofuel production. Among these resources, 103 million dry tons of forestry resources and 241 million dry tons of agricultural resources could be dedicated to biofuel production (Langholtz et al., 2016).

As typical lignocellulosic biomass, agricultural and forestry wastes are primarily composed of cellulose, hemicellulose, and lignin. In the past decades, the utilizations of agricultural and forestry wastes mainly focused on gasification for power generation, briquette fuels production, fermentation for ethanol, and thermochemical conversion for liquid fuels. Hydrothermal liquefaction (HTL) is a thermochemical processing technology that has been extensively investigated for bio-oil production from agricultural and forestry wastes (Jain et al., 2016; Tekin, 2015; Tungal and Shende, 2014). HTL provides several advantages over other techniques. First, this process does not require prior thermal drying and thus results in a reduction of costs for wet materials (Yang et al., 2016). Second, hot pressurized water is used as a reaction medium and reactant. As such, other chemicals are unnecessary; and the whole process is versatile and environmentally friendly (Tekin, 2015). HTL is also less corrosive to equipment than other alternatives (Tungal and Shende, 2014). In a typical HTL process, lignocellulosic materials (LCMs) are depolymerized into bio-oil, biogas, biochar, and water-soluble matter in an aerobic or anaerobic enclosure (Jain et al., 2016; Madsen et al., 2016) (Fig. 1). Purified bio-oils can be used as fuels for burners, stationary diesel engines, turbines and boilers (Duan et al., 2016; Tekin, 2015). Bio-oils can also be further upgraded into transportation fuels (diesel and gasoline) and products, including aromatics, polymers, asphalt, and lubricants (Duan et al., 2016).

In recent years the number of publications on HTL as a promising technology for agricultural and forestry wastes conversion has undergone a sudden increase. However, the generated knowledge is rather fragmentary. Up to now, there is no special review on HTL conversion of agricultural and forestry wastes. For these reasons the current review aims to articulate the research status in HTL of agricultural and forestry wastes, particularly with focuses on the effects of liquefaction conditions on bio-oil yield and the decomposition mechanisms of main components in biomass. The limitations of HTL are discussed and future research priorities are proposed.

2. Composition of agricultural and forestry wastes and their degradation in HTL process

2.1. Composition of agricultural and forestry wastes

Agricultural and forestry biomass comprise plants and plant-based materials, which are specifically called lignocellulosic biomass. Plant cell walls are composed of carbohydrate polymers (microfibrils of cellulose, hemicellulose, and pectin) and other noncarbohydrate polymers, such as lignin (composed of phenylpropane units) and proteins. The main components of lignocellulosic biomass samples are cellulose, hemicellulose, and lignin (Barta and Ford, 2014), which are macromolecules composed of carbon, hydrogen, and oxygen atoms.

Agricultural and forestry biomass is a typical lignocellulosic biomass, which are mainly composed of a variety of complex organic polymers, such as cellulose, hemicelluloses, and lignin (Table 2) (Alhassan et al., 2016; Durak and Aysu, 2016; Doren et al., 2017; Raikova et al., 2016; Yan et al., 2016). Moreover, such biomass also contains a small amount of pectin, nitrogen compounds, and inorganic components. The contents of cellulose, hemicelluloses, and lignin in different agricultural and forestry biomass are summarized in Table 2.

2.2. Brief review on the development of HTL technology

In the early 1970s, Appell et al. (1971), as pioneers in the field, developed the famous PERC (Pittsburgh Energy Research Center) technology. Biofuel production from biomass through HTL received

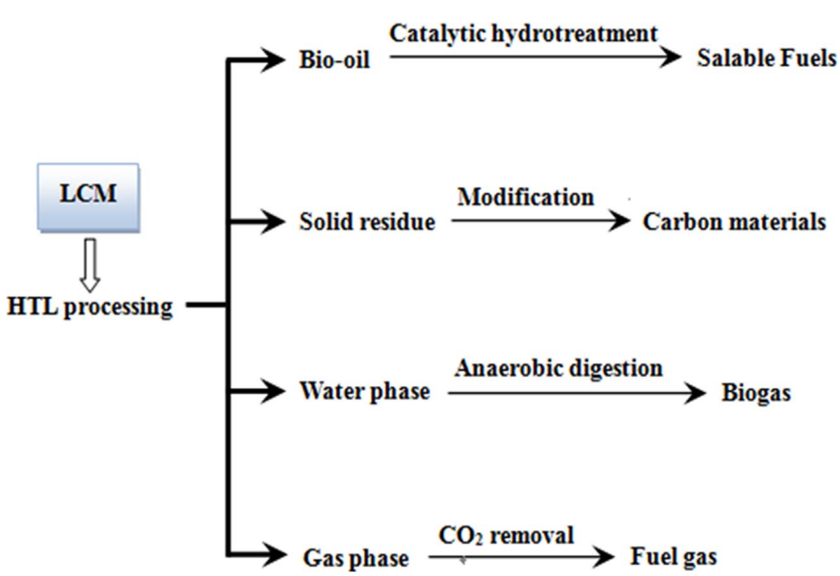

Fig. 1. Scheme of a biorefinery using hydrothermal liquefaction processing and LCMs.