



Efficient utilization of aqueous phase bio-oil to furan derivatives through extraction and sugars conversion in acid-catalyzed biphasic system



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HIGHLIGHTS

- 80% of HMF was extracted from aqueous fraction bio-oil.
- A yield of 72% from HMF and furfural were obtained from bio-oil sugar conversion.
- Addition of DMSO to the biphasic system increased the selectivity towards furfural.

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ABSTRACT

Fractionation, by water addition, is recognized as a strategy for utilization of bio-oil produced from fast pyrolysis process of lignocellulosic biomass. The aqueous fraction was emerged by fractionation which involved water-like and polar compounds such as sugars and furan derivatives. An efficient and selective extraction (80%) of 5-hydroxymethylfurfural (HMF) already existing in the aqueous fraction was performed by using 2-butanone solvent and Amberlyst 16 Wet cation exchange resin. More value-added furan chemicals such as HMF and furfural were produced by the dehydration of sugars in the fractionated aqueous solution. Conversion of sugars into furan derivatives was achieved by using formic acid-catalyzed biphasic system of methylisobutylketone (MIBK) and the aqueous fraction. The conversion process was optimized to produce high furans (HMF and furfural) yield by varying the concentration of formic acid, temperature and time. High furans yield were obtained at high reaction temperature (190 °C) and low acid concentration (0.5 M), or at lower temperature (170 °C) and high acid concentration (1.5 M). The selective production of HMF was favored at high reaction temperature. Modification of the aqueous phase with DMSO addition led to remarkable increase in the yields furan derivatives. The content of DMSO in the aqueous phase was dependent upon the acidity of the aqueous phase and reaction temperature. High DMSO content was preferred at lower formic concentration and higher reaction temperature.

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1. Introduction

The renewable energy resources have been received increasing concern due to the problems of diminishing, global warming, and growing the demand associated with the fossil fuels [1]. Lignocellulosic biomass has been recognized as one of potential sources for variety of fuels, and industrial chemicals [2,3]. Fast pyrolysis is one of technologies used for conversion of lignocellulosic biomass into liquid bio-oil through the thermal decomposition of biomass by rapid heating rate in absence of oxygen [4,5]. The bio-oil yields

ranging from 50% to 80% are dependent on the feedstock, and the pyrolysis conditions such as the temperature, heating rate, and residence time [6,7]. In addition to water, bio-oil consists of a complex mixture of highly reactive compounds, aromatics, short carboxylic acids, phenolics, aldehydes, ketones, sugars, and furan derivatives [8,9]. Due to the complexity of this chemical composition, bio-oil cannot be directly used as fuel, further processing should be carried out to reduce the high oxygen content for production of high quality liquid fuels [10].

Sugars in bio-oil are difficult to be processed via upgrading because of the high tendency of sugars to form undesirable compounds via polymerization or condensation during the heating up time of the upgrading process [11]. Removal of sugars from aromatics is essential to obtain the proper compounds for

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upgrading process of bio-oil [12]. Sugars are more polar compounds than aromatic compounds in the bio-oil. Addition of water, polar solvent, enables the bio-oil to readily separate into aqueous phase and organic phase. The aqueous phase (upper layer) contains mainly the higher polarity components such as levoglucosan anhydrosugars, other sugars (hexoses and pentoses), furan derivatives, organic acids, and low molecular weight phenolics [13,14]. The less polar compounds e.g. syringols, guaia-cols, and high molecular weight phenolics are the main components in the organic phase (lower layer). Sugars in aqueous phase (levoglucosan, hexoses, and pentoses) are recognized as key for production of value-added furan derivatives such as furfural and HMF. The current interest to produce furan derivatives is due to their viable multiple uses in the chemical industries as intermediate compounds between carbohydrates and petroleum-based organic compounds. Furan derivatives can be converted into wide variety of chemicals such as fuel additives and bio-based polymers [15]. The conversion of sugars in the aqueous phase into furan derivatives can enhance the economic perspective for utilization of the aqueous phase. 5-Hydroxymethylfurfural and furfural are the main products of dehydration reaction of different carbohydrates such as fructose, glucose, and cellulose.

There is a variety of different chemicals including high boiling point ionic liquids have been used successfully for the dehydration and conversion of sugars and cellulose into HMF [16,17]. Ionic liquids act as self-catalyzed medium for the dehydration reaction, however, addition of external catalyst is more common to increase the conversion yield. Metal chlorides have been used as catalysts in ionic liquids to achieve high yield of HMF in a short reaction time [18]. In addition to the high price of ionic liquid, the process requires complicated and high energy techniques for HMF separation. Acid catalyzed organic solvents were also used successfully as reaction medium to achieve high yield HMF. Organic solvents can provide many advantages and discourage the formation of insoluble polymers and humins which can be resulted from polymerization of carbohydrates degraded compounds. Also, they can avoid the disadvantages of the pure aqueous medium (acidified water) which can lead to degradation of formed HMF into levulinic and formic acids [19]. Dumesic and his co-workers [20–22] have investigated the use of biphasic reaction systems in which HMF formation can be enhanced in the aqueous phase (water) and also, for simultaneously extraction of the produced HMF by organic solvent (organic phase). The use of biphasic system solves the problem of further conversion of produced furans into undesirable levulinic or formic acids compounds through continuous extraction of furans from the organic phase. Biphasic solvents can also enhance the stabilization and yields of the produced furans. Several inexpensive inorganic acids such as hydrochloric and sulfuric were used as catalysts for dehydration reaction of carbohydrates in biphasic systems. Less corrosive organic acids such as formic was also used to catalyze the conversion processes [23]. Formic acid has other advantages than inorganic acids as it is a by-product in the conversion process with low boiling point allowing easily recycling and reuse as catalyst.

This study aims to maximize the pyrolysis output efficiency by isolating more high-value added chemicals (HMF and furfural) from the aqueous phase bio-oil. In order to accomplish this target we specifically aims to: (1) extracting most of HMF already exist in the aqueous fraction bio-oil and (2) converting aqueous fraction bio-oil sugars to HMF and furfural by using acid catalyzed biphasic system. Optimization of the operating parameters affecting on furans yield such as acid concentration, time and temperature will be performed. The effect of aqueous phase bio-oil modification by addition of dimethyl sulfoxide (DMSO) on the furans yield will be studied as well.

2. Experimental

2.1. Materials

Green pine wood from Southeastern Timber Products LLC (Ackerman, MS) was used in this study to eliminate the cost of drying processes. Debarked green pine wood was crushed to a particle size (3–5 mm) and kept in a cold refrigerator before using. About 250 g from green pine wood were dried, ground between 20–80 mesh sizes and kept in sealed plastic bag for analysis. The results of green pine wood analysis and the used procedures are explained briefly in previous study [12].

2.2. Pyrolysis

The fast pyrolysis of green pine wood was performed in 7 kg/h stainless steel auger reactor located at the Department of Sustainable Bioproducts, Mississippi State University. The biomass sample was fed into the reactor at a temperature 450 °C for 2 s. The heating product gases left the reactor, passed through cooling and separation unit and condensed into bio-oil. The produced bio-oil and solid char were weighed separately after each run to determine the yield of pyrolysis products. The weight and yield of gas was determined by difference. A detailed schematic presentation for the reactor, pyrolysis method, and the calculations of the products yield were described in previous study [24].

2.3. Bio-oil characterization and fractionation step

The bio-oils' physical properties of water content, pH, acid value, viscosity and density were measured for the raw bio-oil (Table 1). Water content was measured by Karl Fisher titration according to the ASTM E203 method. The pH was measured with a pH bench-top meter (Orion 3 star, Thermo Fisher Scientific Inc.). The bio-oil kinematic viscosity was determined by Ubbelohde capillary viscometer at 40 °C water bath temperature according to the ASTM D445 method. The total acid number was determined by dissolving 1 g of bio-oil in an isopropanol/water mixture (35:65) and titrating to a pH of 8.5 with 0.1 N NaOH. The density of bio-oil was determined by Anton Parr DMA 35n portable density meter at 20 °C according to ASTM D 4052 method. The bio-oil was then fractionated into pyrolyginous (organic phase) and aqueous phase using separating funnel by adding equivalent amount of water to the bio-oil. The separating funnel components (bio-oil and water) were mixed thoroughly and left overnight until two distinct layers from aqueous phase (upper layer) and organic phase (bottom layer) were formed. Scheme 1 briefly describes the process of bio-oil fractionation, extraction of HMF originally produced during pyrolysis and conversion of sugars to furan derivatives.

2.4. Extraction of HMF from aqueous phase

The aqueous phase was subjected to solvent extraction treatment in order to extract HMF originally produced during pyrolysis. Extraction treatment was performed by addition 225 mL of

Table 1
Physical properties of raw bio-oil.

Characteristic	Value
Water content	27.6
pH	3.1
Total acid number (mg KOH/g)	81.4
Kinematic viscosity (cSt at 40 °C)	16.3
Density (mg/mL)	1.2

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