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

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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.

Keywords

Fast pyrolysis; Bio-oil; Sugars; Biphasic system; HMF; Furfural

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 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, guaiacols, 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, 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 250g 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 seconds. 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 1g 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 pyrolignous (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 2-butanone to 75 mL of aqueous phase (ratio = 3:1). 2- Butanone solvent was selected for the extraction stage because of its low boiling point. Amberlyst 16 wet cation exchanger (10 % weight/ volume of aqueous phase) was added to the biphasic solution of butanone and aqueous phase to catalyze the extraction stage. The treatment was performed in 450 mL Parr reactor at 120°C for 60 min with 25 min heating-up time. After completion of the treatment, the biphasic solution was filtered using Whatman 42 filter paper to separate the cation exchanger. Filtered biphasic solution was separated into solvent (2-Butanone) layer and aqueous solution (AS) layer by using a separating funnel. The concentration of HMF was determined in both butanone and (AS) layers after the extraction step. After determination of HMF concentration, the butanone solvent containing HMF was subjected to distillation process in the Buchi Rotavapor R-215 at 30°C to separate HMF from butanone solvent.

A highly pure HMF was separated, the purity of HMF was demonstrated by emerging a single HMF peak in HPLC analysis. 2- Butanone solvent can be recycled by further distillation to minimize the water content because butanone and water are partially miscible.

2.5. Hydrolysis of (AS) layer

Acidic hydrolysis process was applied to the (AS) after the extraction treatment in order to convert the anhydrosugars to monomeric sugars. The pH value for the AS after the treatment was measured and a calculated amount from 72% sulfuric acid were added to bring the aqueous solution to 4% according to the standard NREL/TP-510-42623 method [25]. The hydrolysis was performed in an autoclave at 121°C for 1 hour. The hydrolyzed aqueous solution (HAS) been filtrated in a Whatman 42 filter paper to separate the condensed lignin fragments during the hydrolysis process. The (HAS) was neutralized to pH 5.5 by using calcium carbonate followed by analysis of sugars and HMF in the (HAS).

2.6. Biphasic conversion of HAS sugars to furans

Conversion experiments were performed in 70 mL stainless steel reactor. Biphasic solution consisting of 5 mL of HAS and 15 mL of methylisobutylketone (MIBK) with different formic acid catalyst concentrations (0.1- 4 molar) were placed in the reactor and mixed together. The concentration of formic acid used in each run was calculated based on the volume of aqueous phase in the biphasic solution, 5 ml. The reactor was then immersed in a preheated oil bath connected with temperature controller and heater. This point was considered to be the starting reaction time. The conversion experiments were performed at three different temperatures (150, 170 and 190°C) and different reaction times (30-90 min). Experiments with optimum conditions were performed again by adding dimethyl sulfoxide (DMSO) to the HAS/MIBK biphasic system. The total volume of HAS and DMSO was kept constant (5 mL) for each composition and the ratios of HAS to DMSO were 8: 2, 7:3, 6:4, and 5:5. The MIBK volume was also kept constant at 15 mL after DMSO addition. After each run, the biphasic solution was filtered by Whatman 42 filter paper to separate any solid particles from the solution. The filtered biphasic solution was poured in measuring cylinder to

determine the volume of the organic layer (upper layer), and the aqueous layer (lower layer). The two layers were separated by using separating funnel, and filtrated again with 0.2 μm syringe nylon membrane (Millex-GN). HMF and other furans were detected in both organic and aqueous layer by using HPLC.

2.7. Analyses

All sugar analyses in this study were determined according to the standard biomass analytical method described by the National Renewable Energy Laboratory (NREL/TP-510- 42623) method [25]. Standard levoglucosan sugar was added and included in the calibration curve of sugars. Agilent 1200 High Performance Liquid Chromatography (HPLC) instrument equipped with refractive index detector and Biorad column HPX 87P (7.8 mm x 300 mm) was used for sugar analyses at 80°C. Water was used as eluent at flow rate of 0.6 mL/min for 50 min. HMF and furfural analyses were performed by Agilent 1100 HPLC instrument equipped with ZORBAX eclipse C₁₈ Column and UV detector. The column temperature remained constant at 30°C, and the mobile phase was methanol-water (1: 5,v/v acidified by 5% acetic acid) at flow rate of 1.0 mL/min. 10 μL of each sample was injected manually and the concentration of HMF and furfural were detected at 282 nm. HMF and furfural concentrations were calculated based on calibration curve obtained from their standard solutions.

2.8. Calculations

Based on the sugars concentration in [table \(2\)](#), the amount of each sugar in the hydrolyzed aqueous solution (HAS) was calculated as follow:

$$\text{Weight of each sugar (mg)} = \text{Concentration of each sugar (mg/mL)} \times \text{Volume of HAS (mL)}$$

Number of moles for each sugar

$$= [\text{Weight of each sugar in HAS (mg)} / 1000] \times \text{molecular weight for each sugar}$$

The total number of moles (N_t) for sugars in (HAS) was calculated by taking the summation of individual moles for each sugar exist in (HAS).

The weight of each product (HMF and furfural) resulted from sugar conversion in both aqueous and organic layers were calculated as follows:

$$Mp (mg) = [Paq (mg/mL) \times Vaq(mL)] + [Porg (mg/mL) \times Vorg (mL)]$$

206 Where,

207 Mp : Weight of HMF or furfural (mg)

208 Paq : Concentration of HMF or furfural in the aqueous layer

209 Vaq : Volume of aqueous layer produced after the conversion reaction

210 $Porg$: Concentration of HMF or furfural in the organic layer (MIBK layer)

211 $Vorg$: Volume of organic layer after the conversion reaction

212 Number of moles for each product (Np) resulted from the conversion reaction was
213 calculated as follows:

$$Np = [Mp (mg)/1000] / \text{Molecular weight of the product}$$

$$\text{Yield of each product, \%} = [Np/Nt] \times 100$$

214 The total yield for furan compounds resulted from a conversion reaction is the
215 summation of HMF and furfural yield.

216 3. Results and Discussion

217 3.1. Extraction of HMF from fractionated aqueous solution (AS)

218 HMF is one of major compounds existing in the bio-oil produced from the fast
219 pyrolysis process. Soluble organic compounds including HMF, and anhydrosugars, has
220 high tendency toward the aqueous phase emerged through the fractionation of bio-oil.
221 In this study, we applied new approach to extract HMF from the aqueous fraction bio-oil
222 (AS) through applying solvent extraction using (2- butanone) and cation exchange resin
223 (Amberlyst 16 Wet). Extraction of HMF from (AS) can enhance the benefits obtained
224 from the aqueous fraction by minimizing HMF loss during hydrolysis process. **Table (3)**
225 shows the concentration of HMF in (AS) before solvent extraction, and also in both
226 layers (aqueous and butanone) after applying solvent extraction step. It is clear from
227 the table that about 80% of HMF already existing in (AS) was successfully extracted to
228 the organic butanone layer (BL). Pure HMF was recovered from (BL) by gentle
229 distillation at 30°C leaving pure organic butanone solvent that can be reused again. The
230 efficient extraction of HMF may be attributed to the selective adsorption of Amberlyst 16
231 Wet cation exchanger for HMF in the solution. **After diffusion control stage**, HMF can be
232 hold inside the pores of Amberlyst 16 Wet (solid acid) through physical adsorption

forces. Physical bonding can be formed between acidic sites in the cation exchanger and electron-rich sites [single pair of electrons in the oxygen atoms of HMF molecule and conjugated bond system of furan ring]. Also, the electro-binding may be occurred between the anion groups loaded on the substrate of the exchanger and the hydrogen atom (acidic character) of hydroxyl groups in HFM. The adsorption of HMF can facilitate and enhance the efficient extraction of HMF by 2- butanone.

3.2. Effect of formic acid concentration

HPLC analysis for the converted HAS sugars showed two pronounced peaks for HMF and furfural. Fig.1 illustrates the effect of formic acid concentration on the yields of HMF and furfural produced from the conversion of sugars in the (HAS-MIBK) biphasic system at three different reaction temperatures 150, 170, and 190°C for 60 min. The choice of optimum conditions for the effect of temperature and formic concentration was mainly based on the total yield of furan derivatives produced from conversion process. As shown in Fig. 1a–c, the yields of HMF and furfural were gradually increased till reached maxima then decreased with increasing formic acid concentration from (0.1- 4) molar. The concentration of formic acid that gives maxima was highly dependent on the reaction temperature. As shown in Fig. 1a, the reaction temperature 150°C was far below the required temperature to efficiently convert HAS sugars because the highest total yield of HMF and furfural was 23.4% (14.4% HMF and 9% furfural) at 3M formic acid concentration. Increasing the reaction temperature to 170°C led to remarkable increase in the yields of both HMF and furfural compounds at 1.5M catalyst concentration, Fig. 1b. The highest total yield of both HMF and furfural reached to 45.8% and the process was slightly more selective toward the production of HMF (25.5% HMF yield and 20.3% furfural yield). The total yield of furan compounds obtained at 170°C and 1.5M formic was almost twice than that obtained at 150°C and 3M formic. As shown in Fig. 1c, increasing the reaction temperature to 190°C led to more increase in the total furans and the yield reached to 52.7% (39.2% HMF and 13.5% furfural) at 0.5M catalyst concentration. The selectivity of the process toward HMF production became three times higher than the selectivity toward furfural production. Accordingly, we can be concluded from the results shown in Fig. 1a-c that, the reaction temperature had more significant effects than formic acid concentration on

the conversion of sugars in the (HAS-MIBK) biphasic system. The highest total furans yield was shifted toward lower formic concentration with increasing the reaction temperature. This conclusion was supported by the inefficient conversion yield obtained below 170°C even at high formic concentration.

3.3. *Effect of reaction time*

Optimization of reaction time was performed at the optimum conditions determined for temperature and formic acid concentration. Fig. 2a shows the effect of reaction time on the yields of HMF, furfural and their combined yield at 170°C and 1.5M acid concentration. The highest yield for the combined furan derivatives 52.2% (29.6 for HMF and 22.6% for furfural) was obtained at 45 min reaction time. Further increase in the reaction time resulted in gradual decrease in the yield of both HMF and furfural. Therefore, the optimum conversion time for the process at 170°C and 1.5M acid was 45 min. Fig. 2b shows the effect of reaction time on the yields of furan derivatives at the second optimum conditions (190°C and 0.5M acid). The highest yield for the furan derivatives 52.5% (39.2 for HMF and 13.5% for furfural) was obtained at 60 min reaction time. Further increase in the reaction time resulted in gradual decrease in the total yield till 34.2% at 90 min. The decrease in the furan derivatives yield with increasing the reaction time might be related to the conversion of furan derivatives to levulinic and formic acids at the extended time [19]. Therefore, two optimum conversion conditions were selected for further study were (170°C with 1.5 M formic for 45 min) and (190°C with 0.5 M formic for 60 min).

In our previous studies [26-28], we explained the mechanism of conversion of pentoses and hexoses into furfural and 5-hydroxymethylfurfural through acid catalyzed process. Scheme 2 shows the dehydration of pentoses such as xylose into furfural via dehydration reaction in which formation of acid-catalyzed 1, 2-enediol intermediate was formed. This intermediate was subsequently converted into furfural by conjugation and elimination of three water molecules. Scheme 2 shows as well the dehydration reaction of hexoses (fructose, or glucose) in which three water molecules were eliminated. The dehydration of hexoses can go through one of two possible pathways. The first was formation of conjugation for hexose which subsequently was transformed into ring

system followed by stepwise elimination of three molecules of water. The second possible pathway was formation of acyclic intermediates from hexose through the elimination of the three water molecules to form finally HMF. When the dehydration reaction was carried out under vigorous conditions, rehydration or degradation reaction could take place for furfural and HMF to produce unfavorable levulinic or formic acid byproducts. The change of reaction solution color into deep brown after the reaction indicates the formation of soluble polymers and insoluble humin from HMF.

3.4. Effect of DMSO addition in the conversion reaction

The role of phase modifiers aprotic solvents such as DMSO in promoting the efficient production of HMF from carbohydrates was investigated in several previous studies [21, 29]. The presence of DMSO led to increase in the constituent of furanose ring which is formed either from the conversion of pyranose ring (isomerization of glucose to fructose) or from pentoses (xylose) in the reaction medium. The isomerization of glucose to fructose was achieved by the action of the electrophilic and nucleophilic ends of S=O bond existing in DMSO molecule. The effect of DMSO addition was recognized by suppressing the formation condensation byproducts and rehydration of furans produced in the reaction medium by lowering the water concentration in the aqueous phase. Although the hexoses have high tendency to be existed in β -pyranose form, the addition of DMSO could enhance the stabilization of furanose ring form [29, 30] leading to production of more furfural compounds. As a result, DMSO was added in this study to the aqueous phase to improve the selectivity of conversion reaction toward HMF and furfural production via increasing the reactivity of the aqueous phase in the biphasic (MIBK-HAS) system. Addition of DMSO was carried out to form different compositions of aqueous phase (HAS/DMSO = 8:2, 7:3, 6:4, and 5:5) with constant ratio between the organic (MIBK) and aqueous phase (3:1) in the new biphasic process (MIBK-HAS/DMSO). As shown in Fig. 3, the conversion reaction conditions, with addition of DMSO, were performed at the two optimum conditions previously determined. Figure 3a shows the effect of DMSO addition on the yield of conversion products at 170°C. It was found that the addition of DMSO with ratio (7:3) led to highest yields of HMF (39.9%), furfural (31.7%) and total furans (71.2%). On

comparison with the results of conversion without DMSO, the addition of DMSO with (7:3) ratio with HAS enhanced the yields of HMF, furfural and total furans by about 26%, 64% and 36%, respectively. Figure 3b shows the effect of DMSO addition on the yield of conversion products at 190°C. It was found that increasing the ratio of DMSO to the ratio (6:4) resulted in pronounced increase in the yield of furfural from 13.5% to 33.5%. Consequently, the total furan yield was increased from 52.5% to 72.0%. It is obvious that the HAS/DMSO composition (6:4) increased the selectivity of furfural production with more than 100% and total furans with 27.0% compared with the analog experiments without DMSO. Our results are in consistent with the previous results showing the effect of DMSO in shifting the reaction toward more furanose ring formation, furfural.

As shown in Fig. 3, the optimum addition of DMSO was essentially dependent on the acidity of the reaction medium. At reaction temperature 170°C with higher acidity (1.5M), the optimum DMSO addition was achieved with the ratio (7:3). Further increase in the DMSO content to (6:4 and 5:5) led to decrease in the total furans yields. At reaction temperature 190°C with lower acidity (0.5M), the optimum DMSO addition was achieved at higher DMSO content (6:4). Therefore, the acidity of reaction medium should be adjusted to make the addition of DMSO more effective in improving the furans production. The efficient addition of DMSO requires low acid catalyst concentration and high reaction temperature to improve the furans yields produced through biphasic conversion process.

4. Conclusion

This study maximized the benefits of bio-oil aqueous fraction by offering a selective and novel separation technique that succeeded to extract more than 80% of HMF produced from the pyrolysis process. The aqueous fraction bio-oil sugars were recognized as a feedstock to obtain value-added furan derivatives compounds such HMF and furfural. Formic acid catalyzed biphasic reaction system (MIBK-HAS) was used as promising system for performing the dehydration reaction of sugars. The basic process variables that influenced the yields of HMF, furfural and the total furans yield were formic acid concentration, reaction temperature, and reaction time. Based on the

total furans yield, optimization of the hydration reaction was achieved at two different conditions (170°C with 1.5 M formic for 45 min) and (190°C with 0.5 M formic for 60 min). The highest HMF, furfural and total furan yields obtained at 170°C were 29.6%, 22.6% and 52.2%, respectively. The highest HMF, furfural and total furan yields obtained at 190°C were 39.2%, 13.5% and 52.5%, respectively. The selective production of HMF was favored at high reaction temperature. Modification of the aqueous phase by adjusted DMSO addition led to remarkable increase in the yields of furanose ring product (furfural) and accordingly in the total yield of furan derivatives. The content of DMSO in the aqueous phase was dependent upon the acidity of the aqueous phase and reaction temperature. At 170°C and 1.5M acid, addition of DMSO with (7:3) ratio led to highest yields of HMF (39.9%), furfural (31.7%) and total furans (71.2%). At 190°C and 0.5M acid, addition of DMSO with (6:4) ratio led to highest yields of furfural (33.5%) and total furans (72.0%).

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References

- [1] "Hard Truths" About global energy detailed in new study by the national petroleum council. Washington, D.C.; 2007.
- [2] Tilman D, Socolow R, Foley JA, Hill J, Larson E, Lynd L Pacala S, Reilly J, Searchinger T, Somerville C, Williams R. Beneficial biofuels-the food, energy, and environment trilemma. *Science* 2009;325:270-1.
- [3] Somerville C, Youngs H, Taylor C, Davis SC, Long SP. Feedstocks for Lignocellulosic Biofuels. *Science* 2010;329:790-2.
- [4] Oasmaa A, Solantausta Y, Arpiainen V, Kuoppala E, Sipila K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* 2010;24:1380-8.
- [5] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 2004;18:590-8.
- [6] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers Manage* 2006;48:87-92.

- [7] Ingram L, Mohan D, Bricka M, Steele P, Strobel D, Crocker D, Mitchell B, Mohammad J, Cantrell K, Pitmann CU. Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils. *Energy Fuels* 2008;22:614-25.
- [8] Yanik J, Kornmayer C, Saglam M, Yueksel M. Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. *Fuel Process Technol* 2007;88:942-7.
- [9] Hassan E, Steele PH, Ingram L. Characterization of fast pyrolysis bio-oils produced from pretreated pine wood. *Appl Biochem Biotechnol* 2009;154:182-92.
- [10] Maggi RE, Elliott DC. Upgrading overview. Blackie; 1997. p. 575-88.
- [11] Bennett NM, Helle SS, Duff SJB. Extraction and hydrolysis of levoglucosan from pyrolysis oil. *Bioresour Technol* 2009;100:6059-63.
- [12] Hassan E, Abou-Yousef H, Steele PH. Increasing the efficiency of fast pyrolysis process through sugar yield maximization and separation from aqueous fraction bio-oil. *Fuel Process Technol* 2013;110:65-72.
- [13] Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Zacher AH. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. *Environ Prog Sustainable Energy* 2009;28:441-9.
- [14] Scholze B, Meier D. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FTIR, and functional groups. *J Anal Appl Pyrolysis* 2001;60:41-54.
- [15] Gandini A. Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress. *Polym Chem* 2010;1:245-51.
- [16] Liu W, Holladay J. Catalytic conversion of sugar into hydroxymethylfurfural in ionic liquids. *Catal Today* 2013;200:106-16.
- [17] Xiong Y, Zhang Z, Wang X, Liu B, Lin J. Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst. *Chem Eng J* 2014;235:349-55.
- [18] Abou-Yousef H, Hassan E, Steele PH. Rapid conversion of cellulose to 5-hydroxymethylfurfural using single and combined metal chloride catalysts in ionic liquid. *Journal of Fuel Chemistry and Technology* 2013;41:214-22.

- [19] James OO, Maity S, Usman LA, Ajanaku KO, Ajani OO, Siyanbola TO, Sahu S, Chaubey R. Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxymethylfurfural. *Energy Environ Sci* 2010;3:1833-50.
- [20] Roman-Leshkov Y, Dumesic JA. Solvent effects on fructose dehydration to 5-hydroxymethylfurfural in biphasic systems saturated with inorganic salts. *Top Catal* 2009;52:297-303.
- [21] Roman-Leshkov Y, Chheda JN, Dumesic JA. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* 2006;312:1933-7.
- [22] Pagan-Torres YJ, Wang T, Gallo JMR, Shanks BH, Dumesic JA. Production of 5-hydroxymethylfurfural from glucose using a combination of lewis and bronsted acid catalysts in water in a biphasic reactor with an alkylphenol solvent. *ACS Catal* 2012;2:930-4.
- [23] Jiang N, Huang R, Qi W, Su R, He Z. Effect of formic acid on conversion of fructose to 5-hydroxymethylfurfural in aqueous/butanol media. *BioEnergy Res* 2012;5:380-6.
- [24] Tripathi MM, Hassan E, Yueh F-Y, Singh JP, Steele PH. Study of the effect of ultraviolet exposure on bio-oil by laser-induced fluorescence spectroscopy. *Energy Fuels* 2010;24:6187-92.
- [25] Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D. Determination of sugars, byproducts, and degradation products in liquid fraction process samples. National Renewable Energy Laboratory (NREL); 2008.
- [26] Marcotullio G, de Jong W. Furfural formation from D-xylose: the use of different halides in dilute aqueous acidic solutions allows for exceptionally high yields. *Carbohydr Res* 2011;346:1291-3.
- [27] Kuster BFM. 5-Hydroxymethylfurfural (HMF). A review focusing on its manufacture. *Starch/Staerke* 1990;42:314-21.
- [28] Antal MJ, Jr., Mok WSL, Richards GN. Kinetic studies of the reactions of ketoses and aldoses in water at high temperature. 1. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose. *Carbohydr Res* 1990;199:91-109.

444 [29] Amarasekara AS, Williams LD, Ebede CC. Mechanism of the dehydration of D-
445 fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150°C: an NMR study.
446 Carbohydr Res 2008;343:3021-4.

447 [30] Dais P, Perlin AS. Intramolecular hydrogen-bonding and solvation contributions to
448 the relative stability of the β -furanose form of D-fructose in dimethyl sulfoxide.
449 Carbohydr Res 1987;169:159-69.

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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

Table 2

Concentration of sugars (mg/mL) in the hydrolyzed aqueous solution after solvent extraction stage with butanone and (Amberlyst 16 Wet) cation exchange resin.

Sugars	mg/mL
Glucose	43.75
Other Hexoses	8.85
Xylose	9.55
Levoglucosan	17.60
Total sugars concentration	79.75

Table 3

HMF concentration (mg/mL) before and after (Amberlyst 16 Wet) cation exchange treatment

Sample	HMF, mg/mL
Fractionated aqueous fraction before amerlyst 16 treatment (75 ml)	10.26
Aqueous fraction after Amberlyst 16 treatment (75 ml) (AS)	2.04
Organic fraction after Amberlyst 16 treatment (225 ml) (BL)	2.73
Hydrolyzed (4 % sulfuric) Aqueous fraction after Amberlyst 16 treatment (HAS)	0.04

Figure 1:

Figure 2:

Figure 3:

Scheme 1:

Scheme 2:

Figure Caption

Figure 1. Effect of formic acid concentration on the yields of HMF and furfural at different reaction temperatures (Time = 60 min).

Figure 2. Effect of reaction time on the yields of HMF and furfural at the optimum formic acid concentration.

Figure 3. Effect of addition of DMSO to the hydrolyzed aqueous solution (HAS) at the optimum conditions.

Scheme 1. Experimental design showing the steps of HMF extraction from the aqueous solution (AS) and the conversion of sugars into furans derivatives.

Scheme 2. Formation of HMF and furfural from pentoses and hexoses during the acid-catalyzed biphasic processes.