Polymerization on Heating up of Bio-Oil: A Model Compound Study

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Understanding of the condensation reactions in bio-oil is the key for efficient conversion into transportation fuel or value-added chemicals. In this study, the roles of the typical compounds representing the sugars, sugar derivatives, and aromatics found in bio-oil were investigated for their contribution to condensation reactions. Glucose played a key role for the polymer formation due to its decomposition to reactive compounds with multiple hydroxyl groups, carbonyl groups or conjugated π bonds. The sugar derivatives, including furfural, hydroxyl aldehyde and hydroxyl acetone, were also found to be reactive toward polymerization. The carboxylic acids were shown to be the catalysts for polymerization and formic acid was much more efficient to catalyze polymerization than acetic acid. The phenolic compounds also promoted the acid-catalyzed reactions. Vanillin contains reactive a carbonyl group, leading to its high tendency toward polymerization. In methanol, various kinds of methanolysis reactions dominated, which significantly suppressed the decomposition of glucose and the polymerization of other compounds. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 888–900, 2013
Keywords: bio-oil, polymerization, upgrading, model compounds, stabilization

Introduction

Bio-oil, a liquid product resulting from the fast pyrolysis of solid biomass, is a promising renewable feedstock for production of liquid fuels for vehicles.[1–3] However, the raw bio-oil is characterized with a number of deleterious properties. Among those, high instability is one of the biggest challenges facing the hydrotreating of bio-oil into transportation fuel.[4,5] During hydrotreatment at elevated temperatures, the hydrogenation and the polymerization of bio-oil are competitive although polymerization occurs relatively faster than the hydrogenation,[6,7] which can cause blockage of the reactor and deactivation of the upgrading catalysts, making the upgrading of bio-oil by conventional petroleum refineries quite difficult.[8–10] Furthermore, the polymerization of bio-oil even occurs at ambient conditions during aging,[11,12] increasing the water content, viscosity, and average molecular weight of bio-oil[13] and, most importantly, the difficulty for its further processing.

The understanding of how and why the polymerization of bio-oil occurs is important to plan for any possible measures to stabilize or transform bio-oils before its further upgrading. Significant efforts have been made to understand the polymerization of bio-oils, especially during aging, and their stabilization via addition of various organic solvents.[14–23] Bio-oil is not a product of thermodynamic equilibrium during pyrolysis or at storage temperatures, and, consequently, the condensation of the oxygenated organic compounds toward equilibrium continues during aging.[14] The condensation of bio-oil during aging were found to accelerate significantly with the increase of reaction temperature, arising from reactions between the reactive components or even with the ambient oxygen to create large molecules.[15,16] Olefins were found to be very important intermediates in the condensation of bio-oils during aging.[17]

Various organics have been used to achieve stabilization of bio-oil. Bakhshi et al. found that when bio-oil was mixed with tetralin, the properties of the bio-oil mixture remain unchanged with time due to the donation of hydrogen from the tetralin, leading to the improvement of bio-oil stability.[18] Czernik et al. investigated the effects of several additives including methanol, ethanol, acetone, and ethyl acetate on the stability of bio-oil during aging. They found that these organic solvents possessed the ability to drastically reduce the aging rate of bio-oil. This aging inhibition effect was due to the hydrogen-bonding of bio-oil with the additives and the chemical reactions between them.[19] Similar results were also observed by others.[20,21] Roy et al. found that the addition of aqueous phase (mainly water) to bio-oil lowered its thermal stability significantly,[22] while Herring et al. found that the char-free characteristic acts to slow down the polymerization process.[23] These existing knowledge significantly expand and deepen our understanding about the polymerization or stabilization of bio-oils, especially during aging. However, due to the extreme complexity of bio-oils, the

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Additional Supporting Information can be found in the online version of this article.

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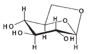
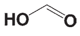
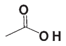
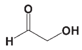
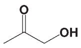
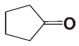
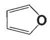
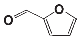
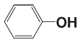
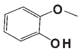
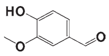
Table 1. Structures of the Model Compounds Employed and their Concentrations in Water Medium or Methanol Medium

Compounds	Structures	Categories	Concentration (wt.%)[a]	Purity
Levoglucosan		Carbohydrates	5	>98%
Formic acid		Carboxylic acids	5	>98%
Acetic acid		Carboxylic acids	5	>99%
Hydroxyl aldehyde		Aldehydes	1	>99%
Hydroxyl acetone		Ketones	5	>90%
Cyclopentanone		Cyclopentanones	5	>99%
Furan		Furans	5	>99%
Furfural		Furans	5	>99%
Phenol		Aromatics	2.5	>99%
Guaiacol		Aromatics	2.5	>98%
Vanillin		Aromatics	2.5	>99%

[a]"Concentration (wt %)" means the concentrations of the compounds in the experiments.

contribution of the main components to the polymerization reactions is still not totally understood. This study tries to better understand the contribution/roles of the sugars, sugar derivatives and aromatics during the polymerization of bio-oil and the effects of methanol on the stabilization of these compounds at elevated temperatures. Understanding this is essential to take the appropriate measures to transform the reactive compounds into more stable ones before hydrotreating the bio-oil.

Most compounds in bio-oil have various oxygen-containing functional groups, which activate these compounds and make the condensation reactions between them very complex. To simplify and get specific information about the reactivity of bio-oil's main components toward polymerization, a series of typical compounds representing the sugars, the sugar derivatives, and the aromatics found in bio-oil were used in this study. Levoglucosan, the anhydrate sugar present in bio-oil in high abundance,[24] was used to represent the sugars in bio-oil. Formic acid, acetic acid, hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan and furfural were used as representatives of the sugar derivatives. Phenol and two substituted phenolic compounds, guaiacol and vanillin, were used to represent the phenolics found in bio-oil.

The roles of each compound in the condensation reactions were investigated in detail while their tendencies toward polymerization were compared. Moreover, correlations between their polymerization tendencies and molecular structures were established, giving us a deeper understanding of polymerization of the whole bio-oil upon heating up. In addition, a methanol medium was employed to stabilize the reactive compounds and the detailed mechanisms were similarly investigated.

Experimental

Materials

The chemicals used in this study were purchased from Sigma Aldrich, Merck Australia, LC Scientific, Inc. (Canada), and Carbosynth Limited (U.K.), respectively. The structures and commercial details about the compounds used in this study are presented in Table 1. The commercially available solid acid catalyst Amberlyst 70 (Rohm and Haas) was used directly in some experiments.

Experimental procedure

The experiments were performed in a 130 mL Hastalloy batch autoclave reactor (Autoclave Engineers, Division of Snap-Tite, Inc.). Typically, 100 g of the reaction mixture containing the typical compounds diluted with either water or methanol was mixed and loaded into the reactor at room temperature. The specific composition of the reaction mixtures are specified in Tables and Figures of the Results and discussion section. The autoclave was purged with nitrogen three times and heated to the desired temperature with a stirring rate of 500 rpm. Each experiment was performed by increasing the temperature from 90 to 190°C with in increments of 20°C. The residence time at each reaction temperature was 30 min. A sample was taken immediately at the end of the 30 min cycle for each reaction temperature. The initial pressure in the autoclave was 1 bar before heating, and the final pressure was around 20 bars. During the thermal treatment of the model compounds, various polymeric products were formed. The soluble polymer was not able to be quantified, but the insoluble ones could be collected via filtration. After filtration, the polymeric material formed was dried in an oven at 105°C for 4 h, to constant weight.

Table 2. Polymer Formation in the Different Runs

	Special conditions of the runs	Polymer to the total reactants (wt.%)
Run 1[a]	With carboxylic acids in water medium	14.7
Run 2[b]	Without carboxylic acids in water medium	3.4
Run 3[c]	Without carboxylic acids and the phenolics	2.3
Run 4[d]	In the methanol medium	4.6

[a]Experimental conditions: Reactants (All the compounds listed in Table 1 plus water): formic acid, acetic acid, levoglucosan, hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan, furfural, phenol, guaiacol, and vanillin. Reaction medium: water. Temperature: from 90 to 190°C with 30 min of residence time at each reaction temperature.

[b]Experimental conditions: Reactants (Without the acids): levoglucosan, hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan, furfural, phenol, guaiacol, vanillin, and water. Others were same to that in Run 1.

[c]Experimental conditions: Reactants (Without the acids and the phenolics): levoglucosan, hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan, furfural, and water. Others were same to that in Run 1.

[d]Experimental conditions: Reaction medium: methanol; Catalyst: Amberlyst 70 (3 wt %); the reactants were all the compounds listed in Table 1 plus methanol. Other reaction conditions were same as that in Run 1.

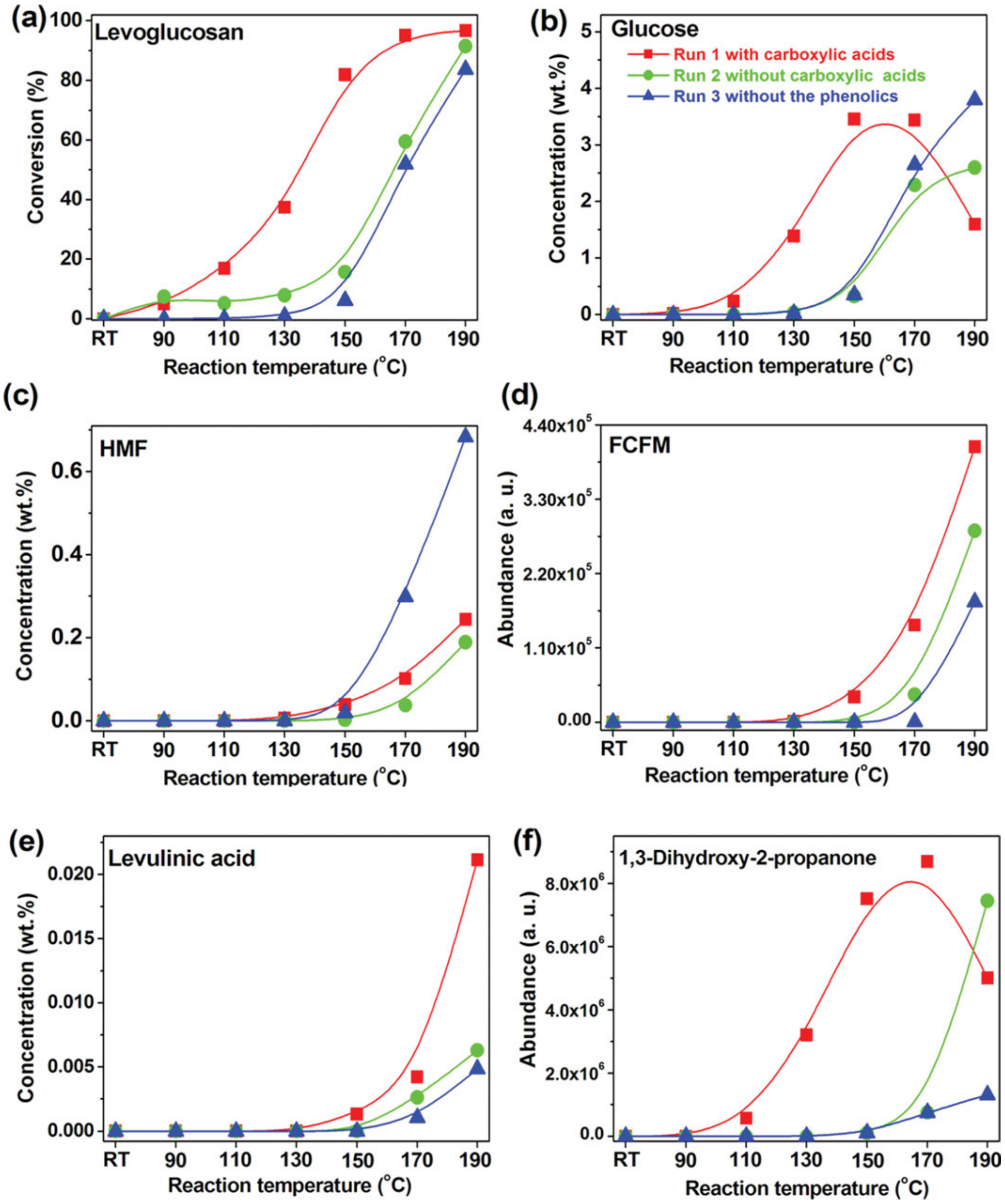


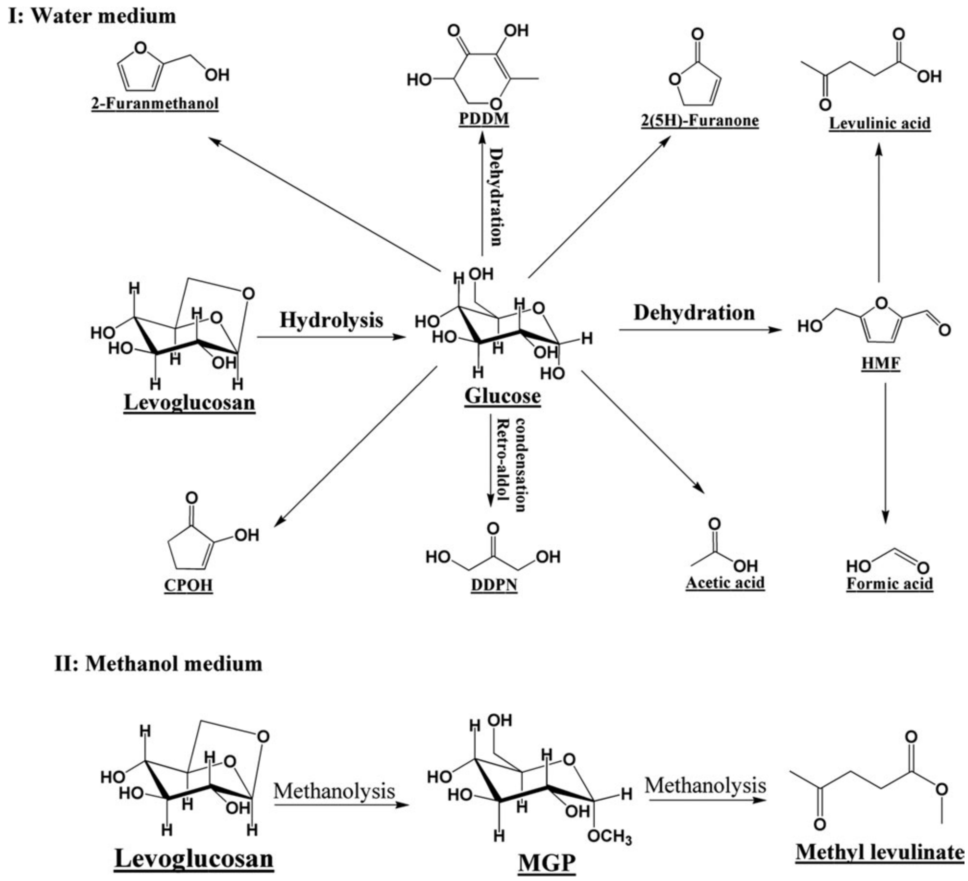
Figure 1. Conversion of levoglucosan vs. temperature.

Reactants in Run 1: all the compounds in Table 1. Run 2: all the compounds in Table 1 with the exception of formic acid and acetic acid. Run 3: all the compounds in Table 1 with the exception of formic acid, acetic acid, phenol, guaiacol and vanillin. The residence time for each reaction temperature was 30 min. HMF: 5-(Hydroxymethyl) furfural; FCFM: 2-Furancarboxaldehyde, 5-(2-furanylmethyl)-. In Figure 1b and 1f there was one point showing a decrease in abundance, which might be not reliable. Thus, repeated experiment was performed and the results were confirmed (Figure S1 in Supporting Information). 218 × 250 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Analytical methods

The products were analyzed using an Agilent GC—MS (6890 series GC with a 5973 MS detector) with a capillary column (HP-INNOWax) (length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 μm of crosslinked poly(ethylene glycol).). One μL of sample was injected into the injection port set at 250°C with a split ratio of 50:1. The column was operated in a constant flow mode using 2.0 mL min^{-1} of helium as the carrier gas. The column temperature was initially maintained at 35°C for 1.8 min before increasing to 260°C at a heating rate of 10°C min^{-1}. The identification of each compound was achieved based on matching its mass spectrum with that in the spectral library and was confirmed by injecting the standards when available. Standard solutions covering the concentration range of the samples were used to obtain the calibration curves for calculating the concentrations of the compounds of interest. It was not possible to obtain standards for all the compounds identified. Thus, the signal intensity (peak area) of the compound was used to measure the changes in their concentration as a function of reaction conditions. The compounds with only the abundance in figures were the ones without the standards available.

A derivatization method was used to determine glucose; broadly following the procedures in the literature.[25] 1-Methylimidazole was used as the solvent and catalyst for the derivatization. Hydroxylamine hydrochloride and acetic anhydride



Scheme 1. Reaction pathways of levoglucosan in the water medium and in the methanol medium. PDDM: 4Hpyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl; MGP: methyl α-D-glucopyranoside; HMF: 5-(hydroxymethyl)furfural. 269 × 245 mm (150 × 150.

were used to react with glucose to form the derivatization product, d-gluconononitrile 2,3,4,5,6-penta-o-acetyl. Deionized water was used to wash away the unconverted acetic anhydride while chloroform was used to extract the product for GC/MS analysis. Repeated experiments were performed and the typical standard deviation was within ±5%.

The definition of conversion of the model compounds is as follows:

Conversion (mol %) = (1 − moles of the model compound in product/moles of the model compound loaded in reactor) × 100%.

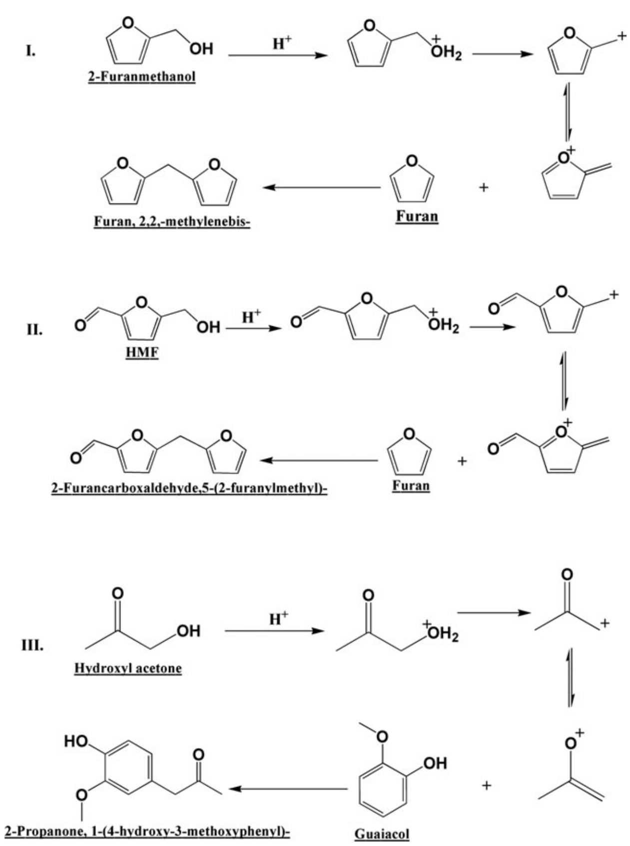
Results and Discussion

Condensation reactions of the typical compounds in the water medium

Many condensation reactions are catalyzed by acids. Carboxylic acids such as formic acid and acetic acid are generally found in bio-oil to varying degrees. Thus, an experiment in the presence of carboxylic acids (Run 1), and another experiment in their absence (Run 2), were performed separately to investigate the roles of carboxylic acids in the condensation reactions. In addition, the phenolic compounds are weak acids, which may also catalyze the polymerization reactions. Hence, another experiment without the presence of carboxylic acids and phenolic compounds (Run 3) was performed to investigate the roles of the phenolics in the condensation reactions. Moreover, the acid-treatment of these model compounds in a methanol medium (Run 4) was performed to investigate the solvent effects of methanol on the polymerization. To elucidate the roles of formic acid and acetic acid in the condensation reactions, two more experiments (Run 5 with acetic acid only and Run 6 with formic acid only) were performed, results of which are presented online in the Supporting Information. The polymers formed in the various experiments are presented in Table 2. The polymer formation of Run 1, with the carboxylic acids, was the most significant while much less was produced in Run 2, without any carboxylic acids. The polymer formation was even less in Run 3, without the phenolics. The polymer formation was significantly suppressed in Run 4 in methanol. The different model compounds played quite different roles in the formation of the condensation products, as discussed later in more detail.

Levoglucosan

Levoglucosan mainly underwent hydrolysis to form glucose in the water medium, as shown in Figure 1. In the case of Run 1, where formic acid and acetic acid were present, hydrolysis occurred above 90°C and accelerated at higher temperatures (Figure 1a and 1b). In comparison, in the absence of carboxylic acids (Run 2), the hydrolysis of levoglucosan proceeded much slower, especially below 150°C. However, the hydrolysis rate of levoglucosan in Run 2, with the phenolics, was somewhat quicker than that of Run 3 without the phenolics, indicating that the presence of phenolic compounds facilitated the hydrolysis of levoglucosan, even though phenolics are weak acids.



Scheme 2. Typical condensation reactions in acid-treatment of the selected model compounds. HMF: 5-(hydroxymethyl)furfural.

With the increase of reaction temperature, glucose, the primary product from the hydrolysis of levoglucosan, further degraded to various products via dehydration, retro-aldol condensation, and decomposition, as shown in Scheme 1. 5-(Hydroxymethyl)furfural (HMF) is a main product from glucose dehydration and it is known that the presence of acids can facilitate the dehydration of glucose to HMF. However, much lower concentration of HMF was formed in Run 1 and Run 2 than in Run 3 (Figure 1c). Evidently, the HMF formed in Run 1 and Run 2 was further converted to other products. The formation of higher concentrations of 2-furancarboxaldehyde, 5-(2-furanylmethyl)- (FCFM) (Figure 1d and Scheme 2), a possible condensation product from HMF and furan, might be one of the reasons for the lower concentration of HMF in Run 1 and Run 2. In the presence of acids, upon addition of a hydrogen ion to the hydroxyl group of HMF followed by dehydration, a carbocation would be formed from HMF, which would attach furan via the electrophilic substitution reaction to form FCFM, as shown in Scheme 2. The electrophilic substitution reaction is catalyzed by acids.[26] Thus, although high concentration of HMF was produced in Run 3, the amount of FCFM formed was remarkably less in the absence of the acids.

In addition to the condensation with furan, HMF also underwent further hydrolysis to levulinic acid (Figure 1e) and formic acid,[27,28] especially in the case of Run 1. The formation of these acids would in return accelerate the hydrolysis of HMF. In addition to the above products, glucose also underwent retro-aldol condensation to 1,3-dihydroxy-2-propanone (Figure 1f).[29] The formation of 1,3-dihydroxy-2-propanone was very sensitive to the presence of acids. Without the acids in Run 3, glucose was relatively stable and the amount of 1,3-dihydroxy-2-propanone formed was quite small. Moreover, the production of 1,3-dihydroxy-2-propanone decreased in Run 1 with the increasing temperature to 190°C. 1,3-Dihydroxy-2-propanone contains both the carbonyl group and the hydroxyl groups, which make its α-H very reactive. It is probable that 1,3-dihydroxy-2-propanone reacted with each other or with other ketones or aldehydes via aldol condensation reactions to form polymers. In addition to 1,3-dihydroxy-2-propanone, many other products such as 4H-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl (PDDM) and 2(5H)-furanone were also formed from the dehydration or decomposition of glucose (Scheme 1). These compounds also contain multiple reactive functional groups, making them quite reactive toward polymerization.

Hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan, and furfural

Hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan, and furfural are all derivatives of sugars. These compounds contain different functional groups that might play different roles during condensation. Hydroxyl aldehyde and hydroxyl acetone contain a hydroxyl group, a carbonyl group, and an active α-H, making them reactive in both the electrophilic substitution and aldol condensation reactions (Figure 2a and 2b). The addition of a hydrogen ion to the hydroxyl groups followed by dehydration would result in the formation of a carbocation. The carbocation might attack any compounds possessing high electron density. One example is the formation of 1-(4-hydroxyl-3-methoxyphenyl)-2-propanone from hydroxyl acetone and guaiacol (Scheme 2). Both the electrophilic substitution and aldol condensation reactions are catalyzed by acids. Hence, significant conversions of hydroxyl aldehyde and hydroxyl acetone were observed in Run 1, in the presence of the carboxylic acids.

In comparison, cyclopentanone contains a single carbonyl group, which was found to be relatively stable, especially in Run 2 and Run 3 without the carboxylic acids (Figure 2c). However, in bio-oil, the structures of the cyclopentanones are more complex. Most of them contain carbon double bonds, carbonyl groups or hydroxyl groups, which will activate them toward polymerization. The formation of 2-(4-methyl-2-furyl)-2-cyclopenten-1-one, a condensation product from cyclopentanones and furans, in Run 1 constitutes an example (Scheme 3, Figure S2 in Supporting Information).

Furan and furfural contain furan ring with high electron density, making them good targets for the electrophilic reagents, as mentioned early in Figure 1d regarding the formation of FCFM. In Run 1 with acids, the conversion of furan and furfural started as low as 110°C and most of them were converted by the end (Figure 2d and 2e). In Run 2 and Run 3, the absence of carboxylic acids slowed the conversion of furan and furfural but significant conversions (ca. 50% in Run 2 and ca. 30% in Run 3) were still achieved by the end of the experiment. The condensation products from furfural polymerization could not be identified by GC/MS, but 2,2′-methylenebis-furan, a product possibly formed from furan and 2-furylmethanol via electrophilic substitution, was detected (Figure 2f and Scheme 2). 2-Furylmethanol was a product from the decomposition of glucose, which might undergo dehydration to the carbon cation (Scheme 2). The further reaction of the carbon cation with the furan would form 2,2′-methylenebis-furan. The production of 2,2′-

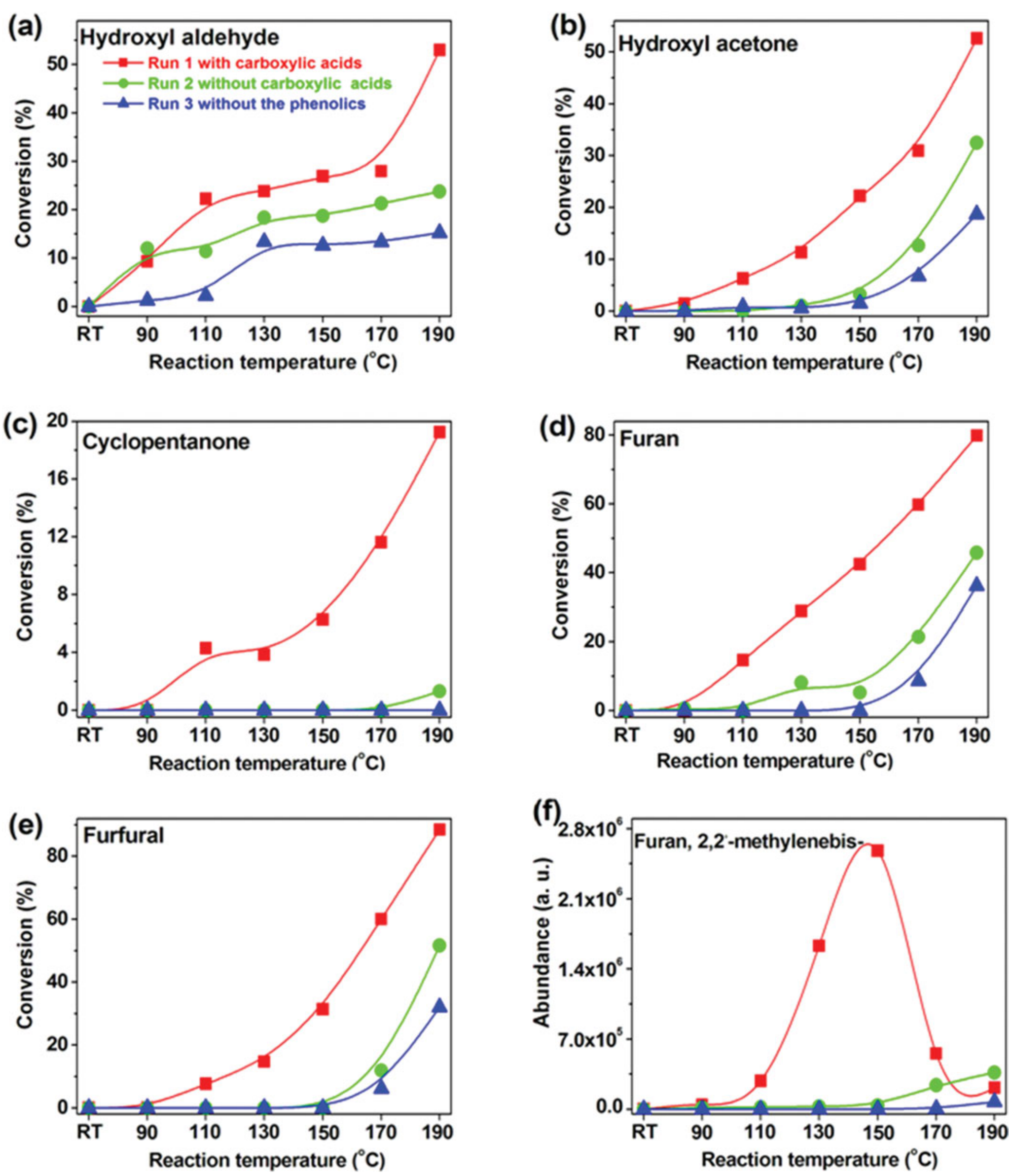
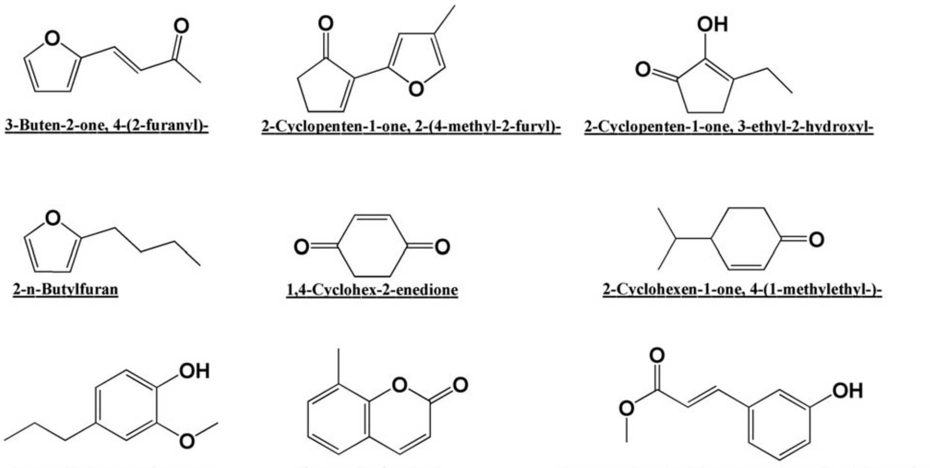


Figure 2. Conversion of hydroxyl aldehyde, hydroxyl acetone, cyclopentanone, furan and furfural vs. temperature.

Reactants in Run 1: all the compounds in Table 1. Run 2: all the compounds in Table 1 with the exception of formic acid and acetic acid. Run 3: all the compounds in Table 1with the exception of formic acid, acetic acid, phenol, guaiacol and vanillin. The residence time for each reaction temperature was 30 min. 296 × 324 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. Condensation products from acid-treatment of the model compounds.

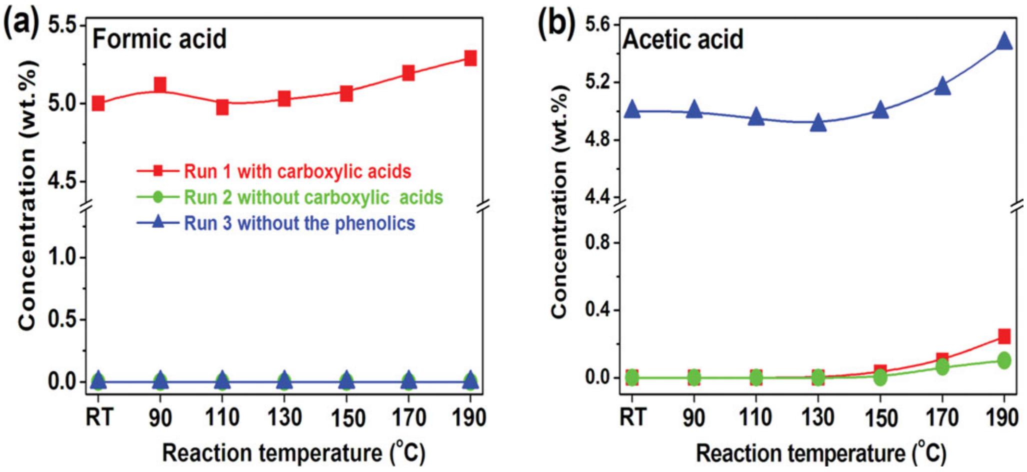


Figure 3. Concentrations of formic acid and acetic acid vs. temperature.

Reactants in Run 1: all the compounds in Table 1. Run 2: all the compounds in Table 1 with the exception of formic acid and acetic acid. Run 3: all the compounds in Table 1with the exception of formic acid, acetic acid, phenol, guaiacol and vanillin. The residence time for each reaction temperature was 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methylenebis-furan was observed to go through a maximum at 150°C. The decrease in its production at the higher temperatures was probably due to its further reaction with other products to form some larger polymeric products.

Acetic acid and formic acid

As mentioned previously, formic acid and acetic acid were efficient catalysts for various condensation reactions. However, formic acid and acetic acid did not directly react

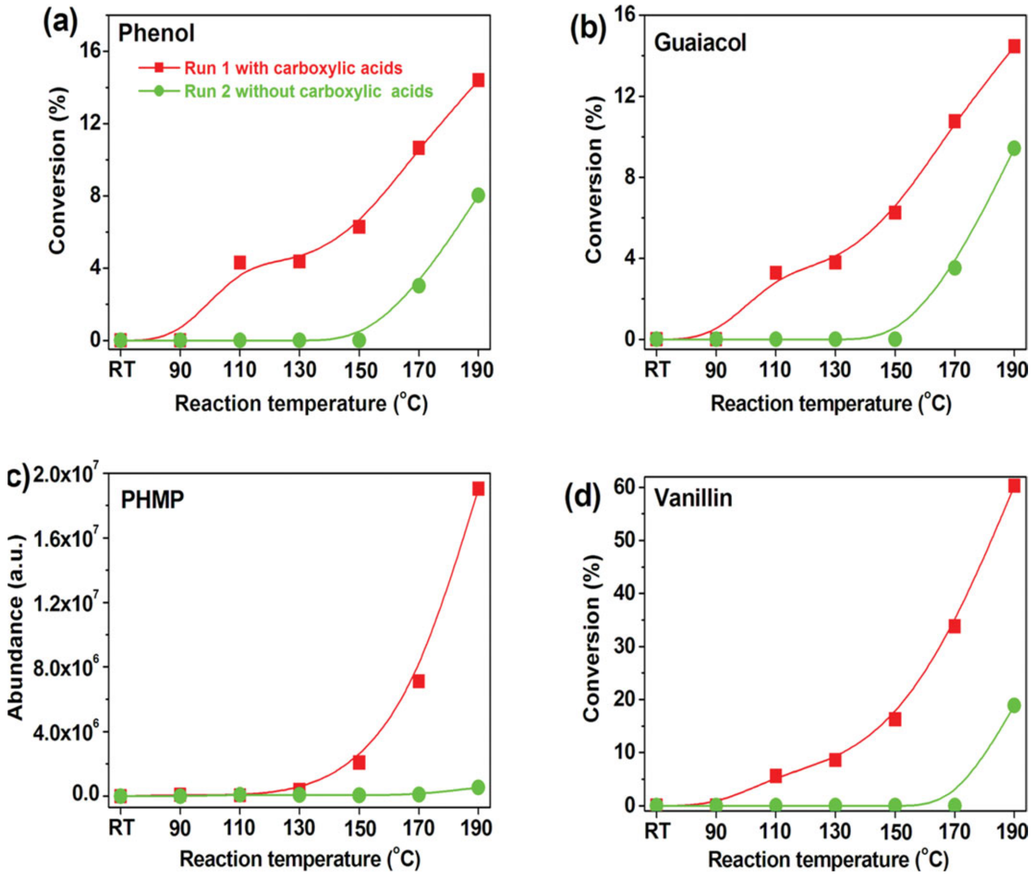


Figure 4. Conversion of phenol, guaiacol, and vanillin vs. temperature.

Reactants in Run 1: all the compounds in Table 1. Run 2: all the compounds in Table 1 with the exception of formic acid and acetic acid. The residence time for each reaction temperature was 30 min 260 × 220 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

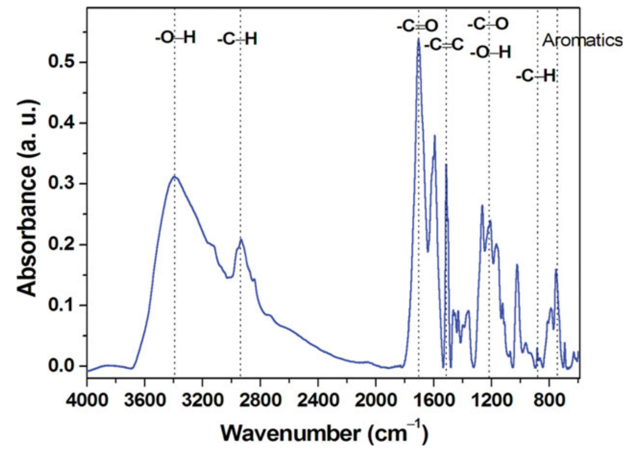


Figure 5. FTIR spectrum of the polymer formed in the acid-treatment of the model compounds during Run 1. 242 × 173 mm (150 × 150 DPI).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with other compounds to form polymer, as seen in Figure 3a and 3b where the concentrations of acetic acid and formic acid vs. reaction temperature even increased to some extent with the elevated temperatures in Run 1. Obviously, some other reactions led to their formation. In Run 2, a small amount of acetic acid was detected above 170°C, which came from the decomposition of glucose (Scheme 1). As for formic acid, it is known that the dehydration of glucose to HMF and the following rehydration and the decomposition of HMF produces levulinic acid and formic acid.[27,28] Both acetic acid and formic acid catalyze the hydrolysis of levoglucosan to glucose and the further decomposition of glucose. Thus, the production of carboxylic acids from the sugar would in return accelerate the hydrolysis and decomposition of the sugar to produce more acids that are the catalysts for the condensation reactions.

Phenolic compounds

The phenolic compounds were found to be reactive in the presence of the carboxylic acids, as shown in Figure 4a and 4b. It is not surprising that the phenolic compounds containing an aromatic ring with high electron density were subject to reaction by the acids which catalyzed their electrophilic substitution. The formation of 2-propanone, 1-(4-hydroxyl-3-methoxyphenyl)- (PHMP) from hydroxyl acetone and guaiacol is a good example (Figure 4c and Scheme 2). In addition, during Run 2, in the absence of the carboxylic acids, small conversions of phenol and guaiacol were still observed

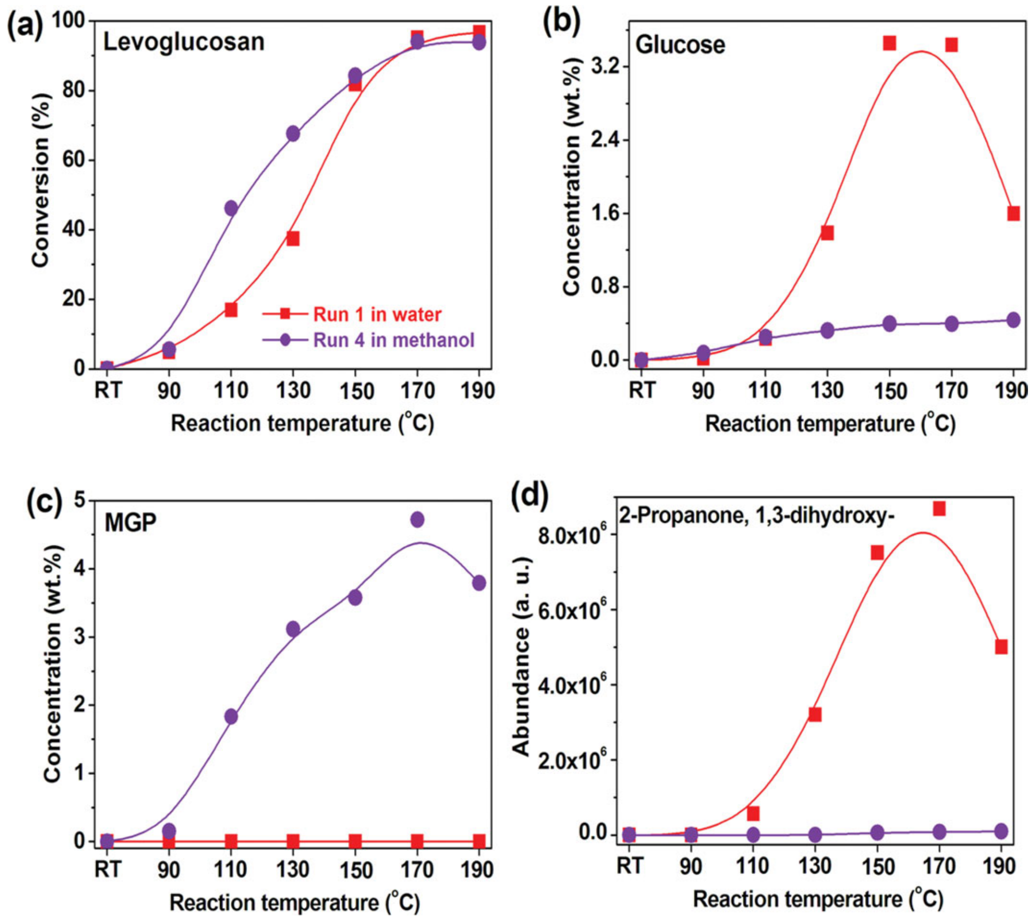


Figure 6. Conversion of levoglucosan vs. temperature in the water medium (Run 1) and in the methanol medium (Run 4).

Reactants in Run 1: all the compounds in Table 1; reaction medium: water. Run 4: all the compounds in Table 1; reaction medium: methanol. Catalyst: Amberlyst 70 (3 wt %). Residence time for each reaction temperature was 30 min. MGP: methyl α-D-glucopyranoside. 262 × 226 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

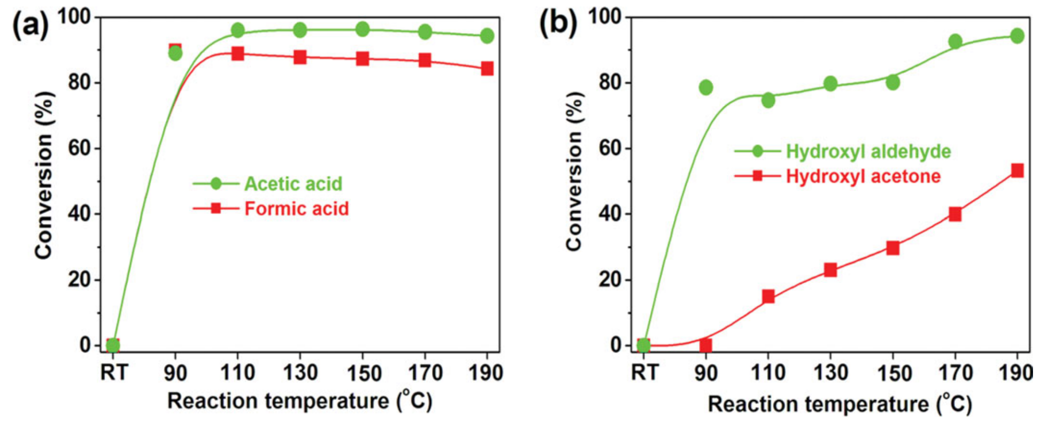


Figure 7. Conversion of acetic acid, formic acid, hydroxyl aldehyde, hydroxyl acetone vs. temperature in the methanol medium (Run 4).

Reactants in Run 4: all the compounds in Table 1; reaction medium: methanol; catalyst: Amberlyst 70 (3 wt %). The residence time for each reaction temperature was 30 min 239 × 97 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when the temperature was raised above 150°C (Figure 4a and 4b), which probably were autocatalyzed since the phenolics are weak acids.

Guaiacol contains an additional methoxy group, but it did not remarkably increase the reactivity of guaiacol. On the other hand, the presence of the carbonyl group in vanillin effectively activated vanillin. It could be seen that in Run 1, with the carboxylic acids, about 60% vanillin was converted (Figure 4d), which is much higher than the conversion rate of phenol and guaiacol (ca. 15%). The presence of the carbonyl group allows vanillin to condense with the sugar derivatives such as the aldehydes and the ketones via the aldol

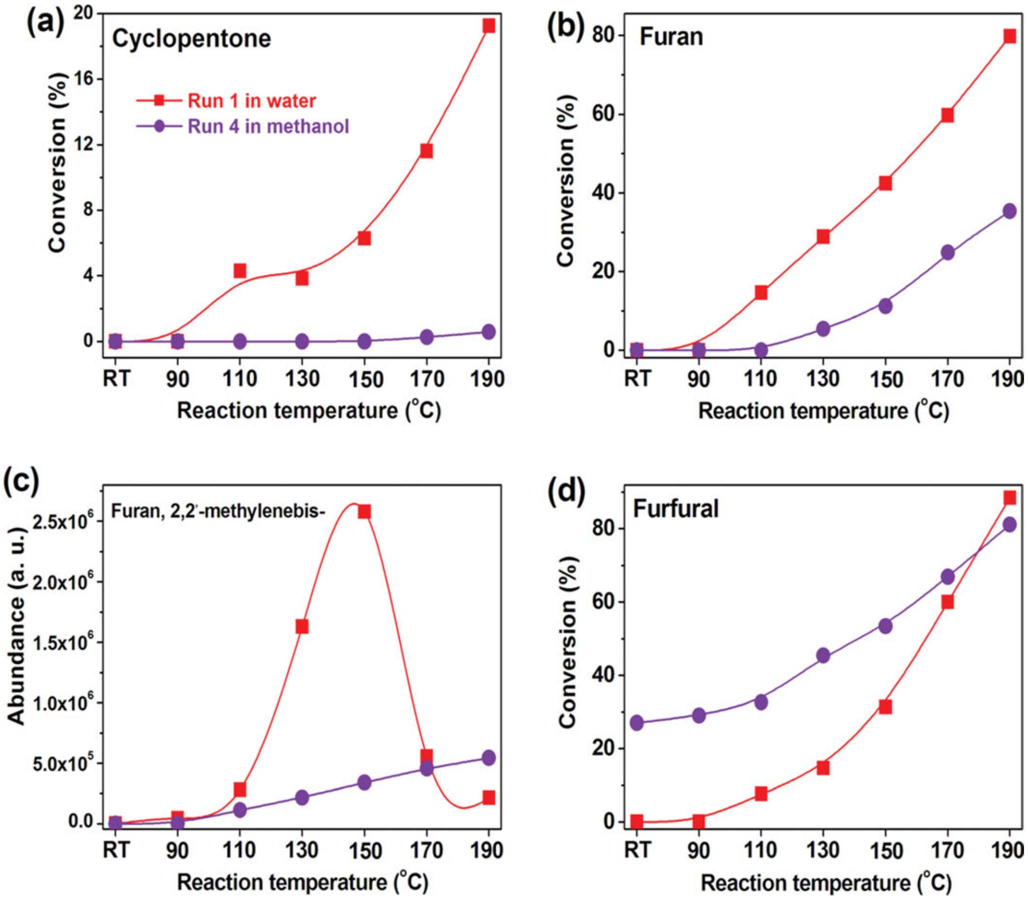


Figure 8. Conversion of cyclopentanone, furan, and furfural vs. temperature in the water medium (Run 1) and in the methanol medium (Run 4).

Reactants in Run 1: all the compounds listed in Table 1; reaction medium: water. Run 4: all the compounds listed in Table 1; reaction medium: methanol; Catalyst: Amberlyst 70 (3 wt %). The residence time for each reaction temperature was 30 min 242 × 201 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

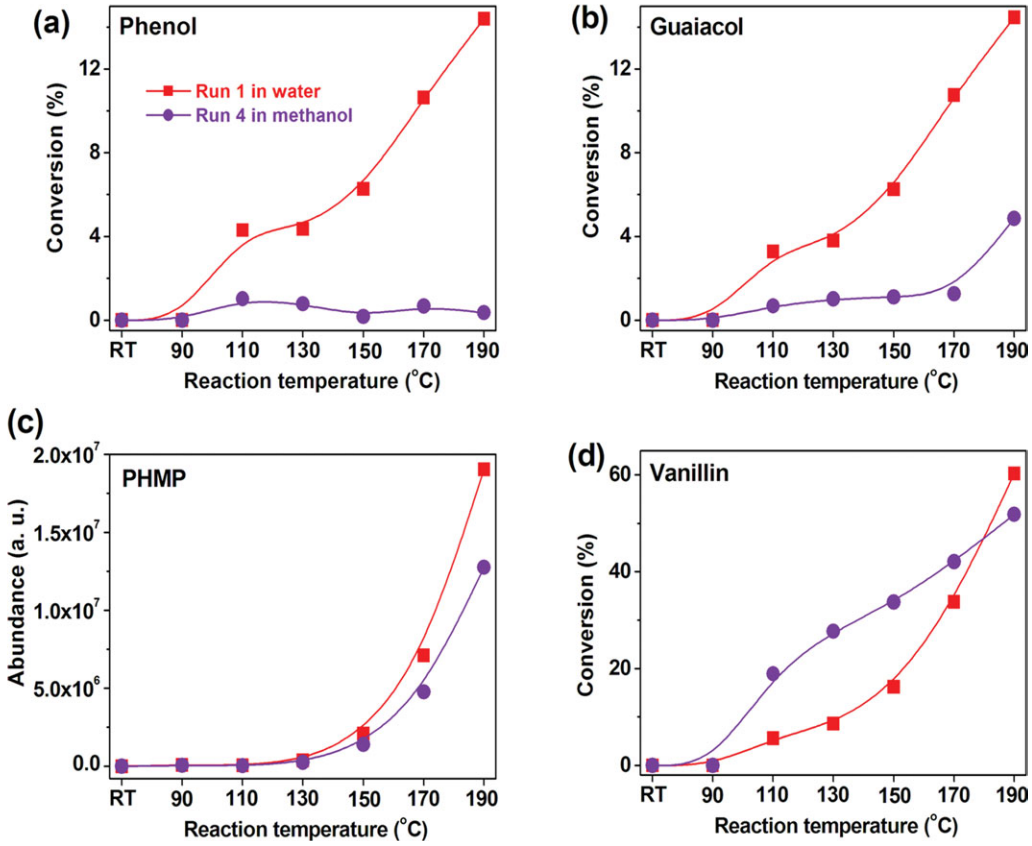


Figure 9. Conversion of phenol, guaiacol, and vanillin vs. temperature in the water medium (Run 1) and in the methanol medium (Run 4).

Reactants in Run 1: all the compounds in Table 1; reaction medium: water. Run 4: all the compounds in Table 1; reaction medium: methanol. Catalyst: Amberlyst 70 (3 wt %). The residence time for each reaction temperature was 30 min. PHMP: 2-propanone, 1-(4-hydroxyl-3- methoxyphenyl)-. 256 × 210 mm (150 × 150 DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

condensation reaction. The reaction of the phenolic compounds with the furans such as furfural was one of the possible reaction pathways for the conversion of the phenolics at high temperatures. It is well-known that with the aid of acid furfural can react with phenolics via electrophilic substitution to form a phenolic resin. The catalysts (carboxylic acids), the phenolics, and the furfural are generally present in the bio-oil obtained from the pyrolysis of wood. Thus, it is very possible that they would react with each other to form such a phenolic resin during the thermal treatment of bio-oil.

Other condensation reactions

The condensation reactions mentioned in Scheme 3 are only a few examples. In fact, the actual condensation reactions were found to be far more complex. Some other condensation products identified have been presented in Scheme 3, but the reaction pathways leading to their formation still needs some clarification. These condensation products generally had large molecular sizes and would react further with the progress of the reaction and eventually form a solid polymer. The solid polymer formed in Run 1 was characterized with FTIR. The spectrum and assignments of the adsorption peaks is presented Figure 5. The characteristic adsorption peaks of the hydroxyl group, the carbon double bonds, the carbonyl group, and substituted aromatic rings can all be found in the spectrum, indicating the involvements of these compounds in the polymerization process.

The polymerization could happen via different ways. As mentioned previously, the electrophilic substitution is one of the main pathways leading to the polymer formation. In addition, the aldol condensation reaction between the aldehydes and/or ketones or even the Diels–Alder reaction between the conjugated diene and the substituted alkene might also occur as these reactions are catalyzed by acids,[31,32] and the reactants were either already present or could have been produced from the decomposition of glucose.

Role of each compound in the condensation reactions

The model compounds played a variety of significantly different roles and presented very different tendency toward polymerization. The carboxylic acids did not directly react with other compounds to polymerize. However, they are the catalysts for the condensation reactions. Formic acid and acetic acid have different pKa (acidity), and they were seen to present quite different capacity to catalyze the polymerization reactions. The conversions of the typical compounds in the presence of formic acid or acetic acid are presented in Figure S3, S4, S5, and S6 in the Supporting Information section.

Levoglucosan tended to undergo hydrolysis to form glucose while glucose continued to undergo dehydration or retro-aldol condensation reactions to form various small compounds (Scheme 1). These small compounds contain multiple functional groups such as hydroxyl group, carbonyl group or conjugated π bonds, which make them very reactive toward their own polymerization or with other products. In addition, the production of carboxylic acids from glucose will in return facilitate the decomposition of glucose and the condensation reactions.

The sugar derivatives presented high susceptibility toward polymerization, especially in the presence of carboxylic acid or even phenolics. Among them, furan and furfural presented the highest tendencies toward polymerization, which was closely related to their conjugated π bonds that are the targets of electrophilic regents. The cyclopentanone was found to be much more stable as it contains only a single carbonyl group. The phenolic compounds are also reactive toward polymerization and, among the three phenolics investigated; vanillin presented the highest tendency to polymerize. In addition, the phenolics also contributed as catalysts for the acid-catalyzed reactions although they were not as efficient as the carboxylic acids to promote polymerization.

Stabilization of the model compounds in methanol medium

As mentioned previously, the carboxylic acids catalyzed the condensation reactions, the removal of which would suppress the polymerizations. Esterification is a well-established method to remove the carboxylic acids with alcohols.[33–45] According to the results of this study it was found that alcohols could react with not only carboxylic acids but also other compounds, contributing to the suppression of the condensation reactions. It can be seen from Table 2 that during the esterification experiment (Run 4) only a small amount of polymer was formed. The detailed mechanism was further investigated.

Compared with what occurred in the water medium, levoglucosan followed very different pathways in the methanol medium. As presented in Scheme 1 and Figure 6, levoglucosan mainly underwent methanolysis to methyl α-D-glucopyranoside (MGP, Figure 6b) with only a small amount of glucose formed (Figure 6c). Moreover, it is very interesting that no 1,3-dihydroxy-2-propanone was detected (Figure 6d). Furthermore, only trace amount of HMF was formed and other dehydration products such as 2-furylmethanol and PDDM could not be detected. Obviously, methanolysis of levoglucosan/glucose to MGP was the main reaction and the dehydration or decomposition of glucose was significantly suppressed. The dehydration or the decomposition products from glucose such as HMF and 1,3-dihydroxy-2-propanone were found to be very reactive contributors to polymerization. The suppression of their formation would effectively inhibit the polymerization reactions from sugars. Our previous study showed that polymer formation from the acid-treatment of levoglucosan could be suppressed effectively in methanol-rich medium, which is due to the protection of the glucose C1 hydroxyl group and the HMF hydroxyl group/carbonyl group.[46] In this study, it was found that the conversion of glucose to MGP could significantly suppress the decomposition of glucose into the reactive smaller molecules, furthering our understanding of the suppressive effects of methanol on the polymer formation from sugars.

In the methanol medium, formic acid and acetic acid could be readily converted to their ester forms above 90°C (Figure 7a). The conversion of hydroxyl aldehyde (Figure 7b) is due to its conversion to 1,1,2-trimethoxyl-ethane via etherification and acetalization (not shown). In comparison, it is difficult to convert hydroxyl acetone to its acetal. In fact, hydroxyl acetone could still react with guaiacol to form a polymer in the methanol medium, as will be shown later.

Cyclopentanone was quite stable in the methanol medium (Figure 8a). Similarly, furan was also much more stable in methanol than in the water medium (Figure 8b) and the formation of furan, 2,2′-methylenebis- was reduced, even in the presence of the solid acid catalyst Amberlyst 70, in Run 4 (Figure 8c). Furfural was initially converted to its acetal, 2-(dimethoxymethyl)-furan, when mixed with methanol at room temperature while 2-(dimethoxymethyl)-furan was further converted at elevated temperatures (Figure S7 in the Supporting Information). The acid-treatment of furfural in methanol at 170°C for 3 h showed that the polymer formation was similar to that formed in the water medium (ca. 55 wt % of polymer to the furfural loaded). The high tendency of furfural toward polymerization was related not only to the furan ring but also to its carbonyl group. Therefore, some pretreatment of furfural, such as the elimination of the functional groups via hydrogenation, may suppress the polymerization of furfural.

The phenolic compounds presented a range of different catalytic behaviors in the methanol medium. Phenol was quite stable (Figure 9a). Guaiacol was not stable above 170°C (Figure 9b), due to the reaction with hydroxyl acetone to form PHMP (Figure 9c), but the conversion rate of guaiacol is much lower in methanol than in water. Vanillin was still very reactive in methanol. Obviously, the carbonyl group served to activate vanillin even in the methanol medium. Some attention needs to be paid to transform or remove the carbonyl group on the aromatic rings to stabilize aromatic compounds such as vanillin.

Conclusions

Based on the results presented previously, some conclusions can be drawn:

1. Sugars play an important role in the polymerization reactions. The anhydrate sugar, levoglucosan, mainly underwent hydrolysis to glucose upon heating up. Glucose is a key compound involved in the polymer formation in the water medium. With the aid of acid, glucose can further undergo dehydration or decomposition into various small compounds which are very reactive toward their own polymerization or with other compounds. In addition, the production of carboxylic acids from glucose in return facilitates the decomposition of glucose and the condensation reactions.

2. The carboxylic acids do not directly react with other compounds to form polymeric products, but they are efficient catalysts for the condensation reactions such as the electrophilic substitution and aldol condensation reactions.

3. Acidity is an important factor in determining the potential of catalyzing the polymerization reactions. Formic acid is much more efficient than acetic acid for the polymerization reactions due to its higher acidity.

4. The phenolic compounds also act as catalysts for the acid-catalyzed reactions although they are not as efficient as the carboxylic acids due to their lower acidity. However, the phenolic compounds directly react with other products to form a polymer due to their conjugated π bonds that are the targets for other electrophilic reagents.

5. Among the sugar derivatives, the furans (e.g., furfural) present the highest tendency toward polymerization, which is

closely related to the furan ring containing the conjugated π bonds and carbonyl groups.

6 Vanillin presents a much higher tendency toward polymerization than phenol and guaiacol due to the presence of a carbonyl group.

7 In the methanol medium, methanolysis of levoglucosan/glucose to MGP significantly suppresses the decomposition of glucose to reactive products, effectively inhibiting the polymerization reactions. The methanol medium can also help to stabilize other typical compounds present in bio-oil, with the exception of furfural and vanillin. Thus, some pretreatments focussed on certain functional groups of highly reactive compounds such as furfural and vanillin are necessary for stabilization.

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Literature Cited

1. Mohan D, Pittman Jr. CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels.* 2006;20:848–889.
2. You F, Tao L, Graziano DJ, Snyder SW. Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input-output analysis. *AIChE J.* 2012;58:1157–1180.
3. Fushimi C, Katayama S, Tasaka K, Suzuki M, Tsutsumi A. Elucidation of the interaction among cellulose, xylan, and lignin in steam gasification of woody biomass. *AIChE J.* 2009;55:529–537.
4. Elliott DC, Hart TR. Catalytic Hydroprocessing of chemical models for bio-oil. *Energy Fuels.* 2009;23:631–637
5. Marquardt W, Harwardt A, Hechinger M, Kraemer K, Viell J, Voll A. The biorenewables opportunity-toward next generation process and product systems. *AIChE J.* 2010;56:2228–2235.
6. Venderbosch RH, Ardiyanti AR, Wildschut J, Oasma A, Heeres HJ. Stabilization of biomass-derived pyrolysis oils. *J Chem Technol. Biotechnol.* 2010;85:674–686.
7. Mercader F, Koehorst PJJ, Heeres HJ, Kersten SRA, Hogendoorn JA. Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. *AIChE J.* 2011;57:3160–3170.
8. Elliott DC. Catalytic hydrothermal gasification of biomass. *Biofuel BioProd Bior.* 2008;2:254–265.
9. Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Zacher AH. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. *Environ Prog Sustain Energy.* 2009;28:441–449.
10. Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels.* 2007;21:1792–1815.
11. Fratini E, Bonini M, Oasmaa A, Solantausta Y, Teixeira J, Baglioni P. SANS analysis of the microstructural evolution during the aging of pyrolysis oils from biomass. *Langmuir.* 2006;22:306–312.
12. Lu Q, Yang X, Zhu X. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. *J Anal Appl Pyrolysis.* 2008;82:191–198.
13. Czernik S, Johnson DK, Black S. Stability of wood fast pyrolysis oil. *Biomass Bioenergy.* 1994;7:187–192.
14. Diebold J. *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils.* In: Bridgwater A, ed. *Fast Pyrolysis of Biomass a Handbook*. Newbury, U.K: CPL Press; 2002.
15. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels.* 2004;18:590–598.
16. Jiang X, Ellis N. Upgrading bio-oil through emulsification with biodiesel: Thermal stability. *Energy Fuels.* 2010;24:2699–2706.
17. Xu F, Xu Y, Lu R, Sheng G-P, Yu H-Q. Elucidation of the thermal deterioration mechanism of bio-oil pyrolyzed from rice husk using fourier transform infrared spectroscopy. *J Agric Food Chem.* 2011;59:9243–9249.
18. Adjaye JD, Sharma RK, Bakhshi NN. Characterization and stability analysis of wood-derived bio-oil. *Fuel Process Technol.* 1992;31:241–256.
19. Diebold JP, Czernik S. Additives to lower and stabilize the viscosity of pyrolysis oils during storage. *Energy Fuels.* 1997;11:1081–1091.
20. Mante OD, Agblevor FA. Storage stability of biocrude oils from fast pyrolysis of poultry litter. *Waste Manage.* 2012;32:67–76.
21. Hilten RN, Das KC. Comparison of three accelerated aging procedures to assess bio-oil stability. *Fuel.* 2010;89:2741–2749.
22. Boucher ME, Chaala A, Pakdel H, Roy C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy.* 2000;19: 351–361.
23. Ortega JV, Renehan AM, Liberatore MW, Herring AM. Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks. *J Anal Appl Pyrolysis.* 2011;91:190–198.
24. Helle S, Bennett NM, Lau K, Matsui JH, Duff SJB. A kinetic model for production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oil. *Carbohydr Res.* 2007;342:2365–2370.
25. Chen CC, Mcginnis GD. The use of 1-methylimidazole as a solvent and catalyst for the preparation of aldononitrile acetates of aldoses. *Carbohydr Res.* 1981;90:127–130.
26. Bellingham P, Johnson CD, Katritzky AR. The mechanism of the electrophilic substitution of heteroaromatic compounds. Part XI. Acid-catalysed hydrogen exchange of α-and γ-pyridones and γ-quinolone. *J Chem Soc B.* 1967;1226–1233.
27. Rosatella AA, Simeonov SP, Frade RFM, Afonso CAM. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* 2011;13:754–793.
28. Rackemann DW, Doherty WOS. The conversion of lignocellulosics to levulinic acid. *Biofuels Bioprod Bioref.* 2011;5:198–214.
29. Rasrendra CB, Makertihartha IGBN, Adisasmito S, Heeres HJ. Green chemicals from d-glucose: Systematic studies on catalytic effects of inorganic salts on the chemo-selectivity and yield in aqueous solutions. *Top Catal.* 2010;53:1241–1247.
30. Kupiainen L, Ahola J, Tanskanen, J. Comparison of formic and sulfuric acids as a glucose decomposition catalyst. *Ind Eng Chem Res.* 2010;49:8444–8449.
31. Baigrie LM, Cox RA, Slebocka-Tilk H, Tencer M, Tidwell TT. Acid-catalyzed enolization and aldol condensation of acetaldehyde. *J Am Chem Soc.* 1985;107:3640–3645.
32. Brion F. On the lewis acid catalyzed diels-alder reaction of furan. regio- and stereospecific synthesis of substituted cyclohexenols and cyclohexadienols. *Tetrahedron Lett.* 1982;23:5299–5302.
33. Xu J, Jiang J, Dai W, Zhang T, Xu Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics. *Energy Fuels.* 2011;25:1798–1801.
34. Mahfud FH, Melin-Cabrera I, Manurung R, Heeres HJ. Biomass to fuels: Upgrading of flash pyrolysis oil by reactive distillation using a high boiling alcohol and acid catalysts. *Process Saf Environ Prot.* 2007;85:466–472:
35. Zhang Q, Chang J, Wang T, Xu Y. Upgrading bio-oil over different solid catalysts. *Energy Fuels.* 2006;20:2717–2720.
36. Moens L, Black SK, Myers MD, Czernik S. Study of the neutralization and stabilization of a mixed hardwood bio-oil. *Energy Fuels.* 2009;23:2695–2699.
37. Li W, Pan C, Zhang Q, Liu Z, Peng J, Chen P, Lou H, Zheng X. Upgrading of low-boiling fraction of bio-oil in supercritical methanol and reaction network. *Bioresour Technol.* 2011;102: 4884–4889.
38. Miao S, Shanks BH, Esterification of biomass pyrolysis model acids over sulfonic acid-functionalized mesoporous silicas. *Appl Catal A Gen.* 2009;359:113–120.
39. Nie J, Chen H, Song Q, Liao B, Guo Q. O-methylation of the phenolic bio-oil with dimethyl carbonate in an ionic liquid [bmim]Cl. *Energy Fuels.* 2010;24:5722–5726.
40. Hilten RN, Bibens BP, Kastner JR, Das KC. In-line esterification of pyrolysis vapor with ethanol improves bio-oil quality. *Energy Fuels.* 2010;24:673–682.
41. Yang X, Chatterjee S, Zhang Z, Zhu X, Pittman Jr. CU. Reactions of phenol, water, acetic acid, methanol, and 2-hydroxymethylfuran with olefins as models for bio-oil upgrading. *Ind Eng Chem Res.* 2010;49:2003–2013.
42. Zhang Z, Wang Q, Yang X, Chatterjee S, Pittman Jr. CU. Sulfonic acid resin-catalyzed addition of phenols, carboxylic acids, and water to olefins: Model reactions for catalytic upgrading of bio-oil. *Bioresour Technol.* 2010;101:3685–3695.

43. Zhang Z, Wang Q, Yang X, Chatterjee S, Pittman Jr. CU. Catalytic upgrading of bio-oil using 1-octene and 1-butanol over sulfonic acid resin catalysts. *Green Chem.* 2011;13:940–949.
44. Zhang H, Carlson TR, Xiao R, Huber GW. Catalytic fast pyrolysis of wood and alcohol mixtures in a fluidized bed reactor, *Green Chem.* 2012;14:98–110.
45. Li X, Gunawan R, Lievens C, Wang Y, Mourant D, Wang S, Wu H, Garcia-Perez M, Li C-Z. Simultaneous catalytic esterification of carboxylic acids and acetalisation of aldehydes in a fast pyrolysis bio-oil from mallee biomass. *Fuel.* 2011;90:2530–2537.
46. Hu X, Li C-Z. Levulinic esters from the acid-catalysed reactions of sugars and alcohols as part of a bio-refinery. *Green Chem.* 2011;13:1676–1679.

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