

# Effect of Methanol on the Liquefaction Reaction of Biomass in Hot Compressed Water under Microwave Energy

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**ABSTRACT:** Liquefaction of sawdust was studied in methanol–water solutions using an acid catalyst under microwave energy. The effect of the methanol concentration on the changes of components in the liquefied products was analyzed by gas chromatography–mass spectrometry (GC–MS). It was found that 5-hydroxymethylfurfural (HMF) and levulinic acid are the dominate products using pure water as the liquefying agent. These two important intermediates are decomposed from glucose by the acid catalyst. When the concentration of the methanol was increased from 0 to 50%, the percentages of HMF and levulinic acid were dramatically decreased from 16.67 and 39.16% to 2.36 and 2.71%, respectively. At the same time, the total content of sugar derivatives increased to 56.96%. This result indicated that methanol could not only improve the conversion of biomass but also promote the stability of the sugar derivatives from further decomposition to carbonyl compounds, such as HMF and levulinic acid. Therefore, a potential polyol product was obtained by a liquefaction reaction using lignocellulosic materials.

## 1. INTRODUCTION

Biomass has been identified as an important source for renewable chemical products and is abundantly available. As an efficient method for biomass conversion, a thermal chemical reaction, such as liquefaction, has been considered as a potential pathway for production of biofuels and chemicals.<sup>1</sup>

In recent years, more attention has been given to liquefaction methods in the presence of solvents, such as water, methanol, and ethanol, because of the simplicity of the process and good quality of liquid products from the process. Different types of biomass have been converted to liquid products by liquefaction, including wood chips, stalks, sawdust, swine manure, domestic garbage, and sewage waste.<sup>2–4</sup>

Studies of liquefaction in the presence of super- or subcritical water have been reported.<sup>5–8</sup> Water is considered the most abundant solvent in the world. Liquefaction of biomass in pure water can be used to produce gas,<sup>9,10</sup> liquid,<sup>11–13</sup> and solid products.<sup>14,15</sup> It should be noted that the catalytic liquefaction of biomass in hot compressed water can be used as an efficient method to produce levulinic acid.<sup>16</sup> On a molecular level, the conversion of a typical lignocellulosic biomass, such as wood or straw, to levulinic acid follows a complicated reaction pathway, involving several intermediate products, such as glucose and 5-hydroxymethylfurfural (HMF).<sup>17</sup> Alcohols have also been proven to be effective solvents for liquefaction of biomass, especially under supercritical conditions.<sup>1,18,19</sup> These hydrophilic organic solvents not only have good solubility for the components decomposed from biomass but can also be easily recovered after liquefaction.

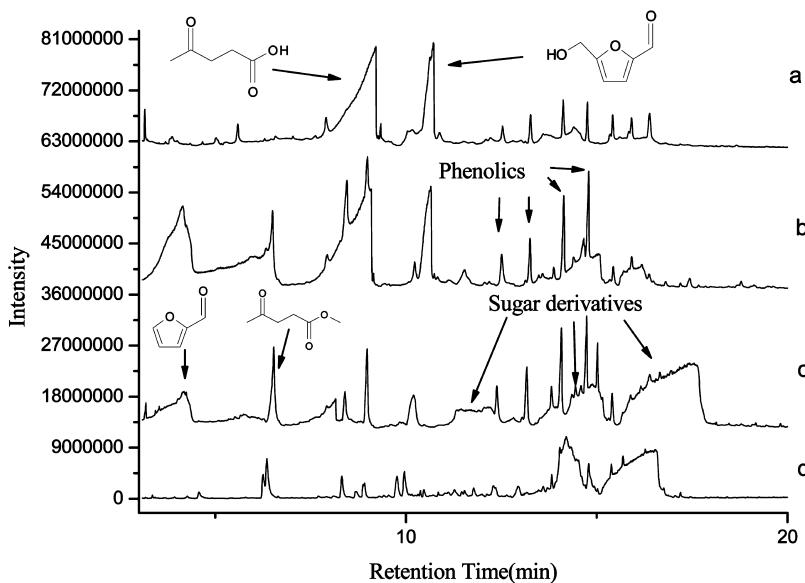
The objective of this study was to investigate the composition of products using different ratios of methanol–water solutions as a liquefying agent. Few studies have reported the mutual effect of water and alcohol on the liquefaction of biomass. It is well-known that methanol could provide good fluidity and permeability at high temperatures during the reaction, which is an important factor to promote the liquefaction reaction. However, the introduction of microwave energy might change the mechanism of the liquefaction. In contrast to conventional heating mechanisms, where energy is first converted to heat and then transferred along temperature gradients from the surface to the core of the material, microwaves induce heat at the molecular level by direct conversion of the electromagnetic field into heat.<sup>20</sup> In our previous work, the liquefied product obtained from conventional heating is a complex mixture of highly oxygenated molecules, which involve a large amount of carbonyl compounds derived from cellulose and hemicelluloses.<sup>21</sup>

In the present study, the preparation of liquefied product by microwave-assisted liquefaction of biomass was investigated. The effect of methanol on the components of the liquefied products was analyzed by gas chromatography–mass spectrometry (GC–MS). The reaction pathway of the liquefaction was also proposed.

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**Figure 1.** Comparison of the GC-MS chromatograms of the products from different concentrations of methanol (a, pure water; b, 25% methanol in water; c, 50% methanol in water; and d, 100% methanol).

**Table 1. Effects of Methanol on the Components of Liquefied Products**

methanol concentration (%)	residue (%)	medium products from the decomposition of cellulose			
		levulinic acid (pentanoic acid, 4-oxo-) (%)	pentanoic acid, 4-oxo-, methyl ester (%)	furfural (%)	HMF (%)
0	51.5	39.16			16.67
25	44.6	26.79	15.35	16.73	7.56
50	37.3	2.71	5.21	6.13	2.36
100	23.7		4.17		

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** The pine (*Pinus sp.*) tree sawdust for this study was produced in the laboratory and pulverized to pass through a 60-mesh sieve, followed by drying at 105 °C overnight. This ground material was kept in sealed bags until needed, at which time, a small sample of the material was dried further in an oven at 105 °C overnight. The elemental analysis for the sawdust was as follows: C (46.61%), H (6.63%), and O (46.76%). The weight percentage of ethanol–toluene soluble matter in the raw material was 8.12% and was defined according to ASTM D1107-96. The weight percentage of lignin in extracted raw materials was 29.25% according ASTM D1106-96. All of the other reagents used in this work were of analytical grade.

**2.2. Liquefaction of Sawdust in Methanol–Water Solution under Microwave Energy.** In a typical operation, liquefaction of biomass was carried out in a Milestone (Shelton, CT) microwave laboratory system equipped with 100 mL of sealed Teflon reaction vessels. This system is especially designed for microwave extraction and was composed of delivered microwave power (1200 W), automatic temperature control with an internal fiber-optic sensor, ASM-400 magnetic stirrer for homogeneous mixing of the sample, maximum operating pressure of 100 bar, and maximum operating temperature of 300 °C.

Samples were irradiated in 5 min under 500 W as the starting microwave power. The sample temperature was controlled at 180 °C. The reaction mixture consisted of 2.0 g of sawdust powder, 8.0 g of water, 8.0 g of methanol, and 0.10 g of catalyst (sulfuric acid) and was mixed with a magnetic stirring during liquefaction. After liquefaction for 15 min, the vessels were allowed to cool at room temperature before opening.

The gaseous products were vented because the yield of gaseous products was negligible. Then, the liquid and solid products were filtered. The solid product was dried at 105 °C for 12 h in an oven and then weighed to give the yield of residue. The residue content was

defined as the percent of the dry weight of residue to the total raw sawdust charged (eq 1).

$$\text{residue content (\%)} = \frac{\text{residue weight (g)}}{\text{weight of raw material (g)}} \times 100\% \quad (1)$$

The filtrate was neutralized with 0.5 M NaOH and then evaporated at 70 °C under vacuum to remove the solvent from the liquid product. The molecular structures and distributions of products from different concentrations of methanol were characterized by GC-MS.

**2.3. Analysis Methods.** The general profile for the biopolymers and phenolic compounds was obtained using electron ionization–mass spectrometry (EI-MS). Analysis of the products was conducted on a mass spectrometer (Agilent 5975C VL MSD), and the products were separated into their components using a gas chromatograph (Agilent 7890A) equipped with a fused capillary column (HP-5,  $L = 30$  m, inner diameter = 0.32 mm, and film thickness = 0.25 μm) with 5% phenyl and 95% dimethylpolysiloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min. The conditions for analysis were as follows: injection mode was split at a split rate of 35, and the column was held at 50 °C for 2 min and then heated to 250 °C at the rate of 10 °C/min, while the injector temperature was 250 °C. The identification of the components of the products was confirmed using total ion chromatograms as well as a fragmentation pattern.

## 3. RESULTS AND DISCUSSION

To understand the effect of methanol on the formation of liquefied products, the compositions of the products were identified and quantified by GC-MS. The components in the liquefied products using different concentrations of methanol are compared in Figure 1. Apparently, the cellulose component in the biomass could be converted into monosaccharides under

Table 2. Selected Organic Components from the Product Using Different Concentrations of Methanol Solutions

peaks	compounds	area (%) <sup>a</sup>			
		100% <sup>b</sup>	50%	25%	0%
1	furfural			6.13	16.73
2	pentanoic acid, 4-oxo-, methyl ester		4.17	5.21	15.35
3	pentanoic acid, 4-oxo-			2.71	26.79
4	levoglucosenone	1.30	0.85		
5	1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose	1.86	0.26		
6	2-furancarboxaldehyde, 5-(hydroxymethyl)-			2.36	7.56
7	$\alpha$ -D-glucopyranoside, methyl	1.79	4.65		
8	$\alpha$ -D-ribopyranoside, methyl	0.40	0.72		
9	$\beta$ -D-ribopyranoside, methyl			2.60	0.54
10	benzaldehyde, 3-hydroxy-4-methoxy-		1.64	1.14	0.88
11	phenol, 2-methoxy-4-propyl-		1.93	1.10	1.59
12	$\beta$ -D-glucopyranose, 1,6-anhydro-		0.42	0.11	
13	D-allose		1.10	0.25	
14	benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	1.21	1.52	0.56	
15	$\beta$ -D-glucopyranose, 1,6-anhydro-	5.61	0.19	0.62	
16	D-allose		0.41	3.44	2.85
17	homovanillyl alcohol		3.15	2.45	1.00
18	ethyl $\alpha$ -D-glucopyranoside		1.47		
19	methyl $\beta$ -D-galactopyranoside	4.16	2.05		
20	ethanone, 1-(4-hydroxy-3-methoxyphenyl)-		3.29	3.07	1.24
21	$\beta$ -D-glucopyranose, 1,6-anhydro-		2.21	0.25	
22	1,1-dimethoxy-2-phenylpropane		2.77		
23	benzene acetic acid, 4-hydroxy-3-methoxy-		1.07	2.88	0.66
24	$\alpha$ -D-galactopyranoside, methyl	61.51	39.44	0.86	
25	hexadecanoic acid, methyl ester		1.51	0.26	
26	$\alpha$ -D-galactopyranosiduronic acid, methyl, methyl ester		0.59	2.17	
27	methyl 6-O-[1-methylpropyl]- $\beta$ -D-galactopyranoside		0.14		
28	9-octadecenoic acid (Z)-, methyl ester		0.23		
29	1-phenanthrenecarboxylic acid, 1,2,3,4,4a,10a-hexahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1 $\alpha$ ,4a $\beta$ ,10a $\alpha$ )]-		0.06		
30	1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1 $\alpha$ ,4a $\beta$ ,10a $\alpha$ )]-		0.08	0.03	
31	octadecanoic acid, 9,10-dihydroxy-, methyl ester		0.07		
32	7-oxodehydroabietic acid, methyl ester		0.11		
33	ethanone, 2-(1H-imidazo[4,5-b]pyridin-2-yl)-1-(4-morpholyl)-		0.09		

<sup>a</sup>Area percent is based on the total ion current. <sup>b</sup>The liquefied product was further extracted by methylene chloride to remove phenolics.

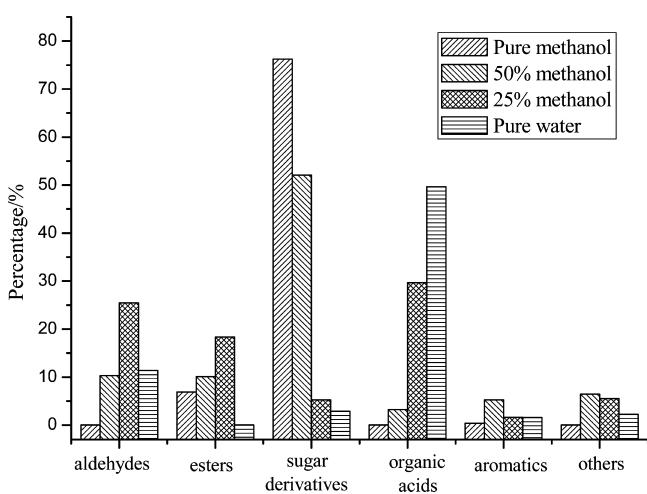
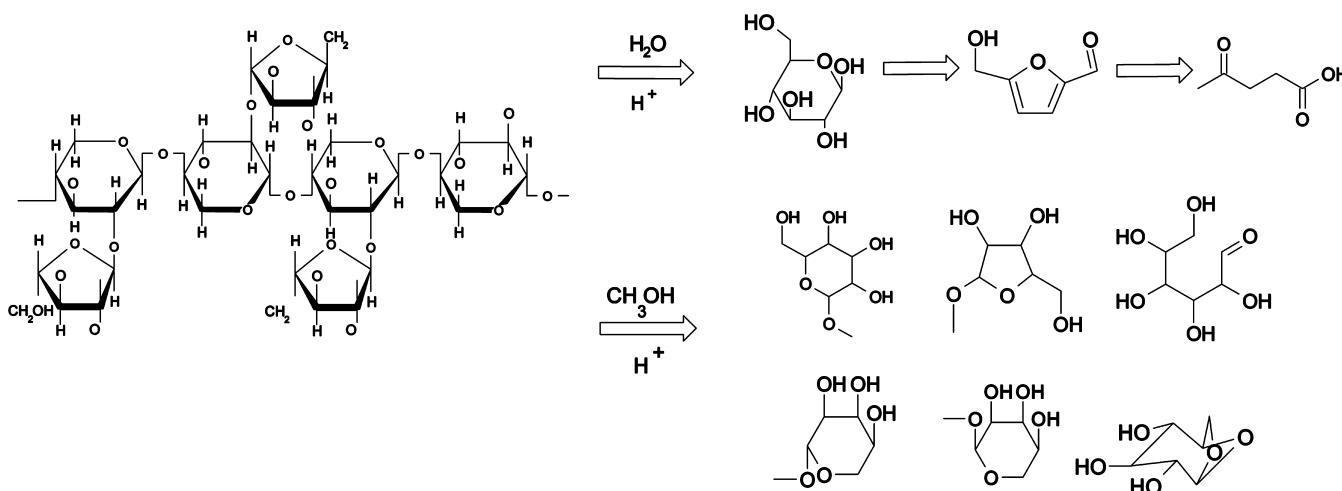


Figure 2. Classification analysis of components identified in GC-MS under different methanol concentrations.

the microwave energy (see the peaks between 12 and 16 min). However, these multi-hydroxy compounds could then be

decomposed into HMF under an acid catalyst in aqueous solution and then further transformed into organic acids, such as levulinic acid (chromatogram a in Figure 1). This is a conventional method for the production of levulinic acid<sup>17</sup> using lignocellulosic biomass.

In this study, a mixture of methanol and water was used as the liquefying agent. We believe that methanol could provide higher autogenous pressure and better solubility for the organic products during the reaction, which is an important factor to promote the liquefaction reaction. From Table 1, it is evident that the percentage of residue decreased from 53.1 to 36.4% with the increasing dosage of methanol. To our surprise, it was also found that the amount of methyl monosaccharides increased significantly, while HMF and levulinic acid decreased with an increased amount of methanol. This result is in good agreement with the observations in chromatograms b and c in Figure 1. When the concentration of methanol was increased from 0 to 50%, the percentages of the two important intermediates, HMF and levulinic acid, decreased dramatically from 16.67 and 39.16% to 2.36 and 2.71%, respectively. Therefore, it could be concluded that methyl monosaccharides



**Figure 3.** Reaction pathway of cellulose in methanol–water solutions.

can prevent the sugar structures from further decomposition to a furfural structure (HMF).

The liquefied product is a dark brown liquid with a mild odor, which has a complex array of components. A GC–MS analysis of the liquefied product using 50% methanol solutions is shown in Table 2.

Table 2 shows that oxygen-containing organic components of liquefied products involve many classes of compounds, such as sugar derivatives, carboxylic acids, alcohols, phenolics, esters, and furfural derivatives. When the product using 50% methanol was taken as an example, the most abundant organic component in the product was methyl  $\alpha$ -D-galactopyranoside. Its peak area was 39.44%, the largest percentage of the oxygenated organic components present. This broad peak may also contain some related monosaccharides. Methyl  $\alpha$ -D-galactopyranoside was generated from the decomposition of cellulose. The glycosidic bond was attacked by methanol OH functions to form multiple kinds of methyl monosaccharides. Other kinds of sugar derivatives were detected, such as levoglucosenone, methyl  $\beta$ -D-ribopyranoside, 1,6-anhydro- $\beta$ -D-glucopyranose, and D-allose. The total content of these sugar derivatives was 56.96%. We believe that this represents a new method for the preparation of methyl sugar derivatives from lignocellulosic materials. It is perfectly suitable for these products to be used as potential platform chemicals, such as polyols, in the polyurethane industry because the appropriate viscosity and hydroxyl number of the final products can be obtained by a slight modification using ethylene oxide and propylene oxide.

Phenolics and aromatics were abundant, including 2-methoxy-4-propyl-phenol, homovanillyl alcohol, and 4-hydroxy-3-methoxy-benzeneacetic acid. These compounds are produced from the decomposition of lignin. They represented about 12.60% of the peak areas.

Several kinds of carbonyl compounds were identified, such as furfural, levulinic acid, and 5-(hydroxymethyl)-2-furancarboxyaldehyde. They were further decomposed from sugars, such as glucose, through isomerization, dehydration, and hydrolysis during the liquefaction reaction.<sup>17</sup> The sum of their corresponding peak areas was 16.41%. Other compounds in the liquefied products included fatty acid derivatives and rosin acid derivatives. These are organic impurities generated by the trees during growth.

On the basis of the GC–MS results, classification of the components is illustrated in Figure 2. The stability of the sugar derivatives significantly improved with greater methanol concentration. Using pure methanol as a solvent, the total content of the sugar derivatives was up to 76.23%. However, the content of sugar derivatives decreased to 2.85% when using pure water. The amount of levulinic acid and their derivatives decreased when using pure methanol, which indicated that the further decomposition of sugars was prevented at the stage of methyl monosaccharides.

The reaction pathway for liquefaction using methanol–water as the solvent was proposed on the basis of GC–MS analysis. The structure of cellulose is merely illustrative and does not imply a particular sequence. Previous studies have shown that cellulose tends to decompose to monosaccharides in water under acid catalysis, which can be further decomposed to form HMF and levulinic acid.<sup>17,18,22</sup> In our observations, methyl monosaccharides generated from lignocellulosic materials has good thermal stability in methanol compared to water. As shown in Figure 3, with increasing amounts of methanol, more methyl sugar derivatives were found in the products, including methyl  $\alpha$ -D-galactopyranoside, methyl  $\beta$ -D-ribopyranoside, 1,6-anhydro- $\beta$ -D-glucopyranose, and D-allose. Alcoholytic of lignocellulosic materials can produce a new multi-hydroxyl product, which has a stable chemical structure during liquefaction processing with an acid catalyst.

## CONCLUSION

The effect of methanol on the chemical changes of liquefied products in hot compressed water was investigated. With the increase of the methanol content, it was found that the methyl sugar derivatives were significantly increased, while two important intermediates, HMF and levulinic acid (generated from decomposition of glucose), were decreased. When the methanol concentration reached 50%, the total content of these sugar derivatives was 56.96%. This indicated that the methyl sugar derivatives have a more stable structure than sugars (such as glucose) in acid catalysis reactions. Further studies of this reaction, such as removing the phenolics and modification of the sugar derivatives using ethylene oxide and propylene oxide, are needed and are currently under investigation in our research group.

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**Notes**

The authors declare no competing financial interest.

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