

Effect of Different Solvents on Cypress Liquefaction to Fuels and Characterization of Products

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This study investigated the effects of various solvents on cypress liquefaction in the range of 180 to 300 °C. The solid residues and bio-oils obtained from cypress liquefaction were characterized to investigate the mechanism of the liquefaction process. Results obtained using FT-IR, sugar analysis, and elemental analysis showed that the solvent could affect both the formation of various compounds in the bio-oil and the product distribution during the cypress liquefaction process. Considering the bio-oil yield, the solvent efficiency in cypress liquefaction was as follows: water > methanol > ethanol. The decomposition velocities of cellulose, hemicelluloses, and lignin were different in the solvents, and hemicellulose decomposition preceded cellulose and lignin in all solvents. Water had the most pronounced effect on the higher heating value (HHV) of residues among the three tested solvents; the highest HHV was 26.3 MJ/Kg. This study suggests that characterization of products provides a promising approach for investigating the mechanism of solvent effects on biomass liquefaction.

Keywords: Liquefaction; Solvent; Solid residue; Bio-oil

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INTRODUCTION

Biomass can be converted into fuels using thermo-chemical and bio-chemical processes, but thermo-chemical conversion technology has become dominant because of the high-efficiency conversion to gaseous, liquid, and solid products under thermal conditions (Zhang *et al.* 2006). There are two typical thermo-chemical processes that produce a liquid product with a high yield: pyrolysis and liquefaction. Pyrolysis is a process in which dry biomass is subjected to rapid heating to a high temperature in an inert atmosphere. The high operating temperature (400 to 1000 °C) of pyrolysis can lead to cross-linking reactions between hydrocarbons and aromatics, resulting in tar. Therefore, it is difficult to further decompose biomass (Zhang *et al.* 2007; Ates *et al.* 2008). Currently, liquefaction is used by many researchers for utilizing biomass because of its advantages, such as (1) the presence of solvent dilutes the concentration of the products, decreasing the opportunity for cross-linked reactions and reverse reactions, and (2) the relatively low temperature in comparison with pyrolysis (Hassan and Shukry 2008; Liu and Zhang 2008; Chen and Lu 2009).

Solvents have a remarkable effect on the liquefaction reaction, and some articles have reported that the liquefaction of biomass in the presence of organic solvents effectively lowers the viscosity of heavy oil derived from biomass liquefaction (Demirbas 2000). Although solvents have shown obvious reactive activity in many works, it is still unclear how solvents affect the biomass liquefaction process. In general, the degradation of biomass cannot be described by detailed chemical reaction pathways with well-defined

single reaction steps. The reason for this is that biomass components interact with each other, leading to a very complex chemistry in the liquefaction process (Kruse and Gawlik 2003). The processes of liquefaction show similarities with the pyrolysis process, but also significant differences, due to the presence of solvents as both the reactant and the reaction medium.

Knowledge of the mechanism of biomass liquefaction may help to better understand the liquefaction process. In spite of significant ongoing research on the characterization of products using FT-IR, NMR, and GC-MS, there is little information on the thermal behavior of various solvents with respect to the products.

Liquefaction of biomass has been carried out with some solvents, but the investigations cannot be compared due to the difference in the separation of products and the lack of studies carried out under identical conditions to understand the effect of solvent on the product distribution and characterization of solid residue. In this paper, the effects of three solvents (water, methanol, and ethanol) on the product distribution were examined utilizing a stainless-steel autoclave. The bio-oil compositions obtained from various solvents were analyzed by GC-MS. In addition, the solid residues obtained from different liquefaction processes were characterized by FT-IR, sugar analysis, and elemental analysis.

EXPERIMENTAL

Materials

Cypress was collected in Xucang, Henan province, China. Samples were air-dried and milled, and particles smaller than 40 mesh were used. The chemical analysis of cypress was performed according to Liu *et al.* (2013). Results showed that the cypress contained 32.2% cellulose, 27.3% hemicelluloses, 38.2% lignin, and 2.3% ash (on a dry basis). All of the chemicals used in this work were of analytical grade.

Experimental Procedure and Characterization

Liquefaction experiments were carried out in a 1000-mL stainless steel cylindrical autoclave (Parr, USA). The details of the experiment and separation products have been described previously (Liu *et al.* 2013).

Briefly, the liquefaction products were filtered to separate the water-soluble fractions (for ethanol and methanol liquefaction tests, the solvent was first removed from the solid and liquid mixture and then 100 mL of de-ionized water was added to the mixture before separation).

After removal of the water under reduced pressure at 85 °C in a rotary evaporator, the aqueous product was designated water-soluble oil (WSO). The water-insoluble fraction was washed with acetone, and the contents were separated by filtration under vacuum. The acetone was evaporated in a rotary evaporator, and this fraction was designated heavy oil (HO). Thus, in this paper, the term bio-oil was defined to be the HO and WSO.

The acetone-insoluble fraction was dried at 105 °C and called the solid residue. The elemental, sugar, FT-IR, and GC-MS analyses of the products were performed as described previously (Liu *et al.* 2013).

RESULTS AND DISCUSSION

Effect of Solvent Type on Product Distribution at Different Temperatures

Liquefaction of cypress with three different solvents (water, ethanol, and methanol) was studied under identical experimental conditions. The bio-oil and solid residue yields from the cypress liquefaction using different solvents at different final temperatures are shown in Fig. 1. Among the three solvents, water had the most pronounced effect on the conversion at all the tested temperatures; the lowest solid residue yields were 29.1%, 53.8%, and 56.6% with water, ethanol, and methanol as solvents, respectively. On the other hand, a slight increase in yield was found when the temperature was increased to 300 °C; the bio-oil (WSO and HO) yield leveled off from 32 to 29.4% when the temperature was increased from 280 to 300 °C in water.

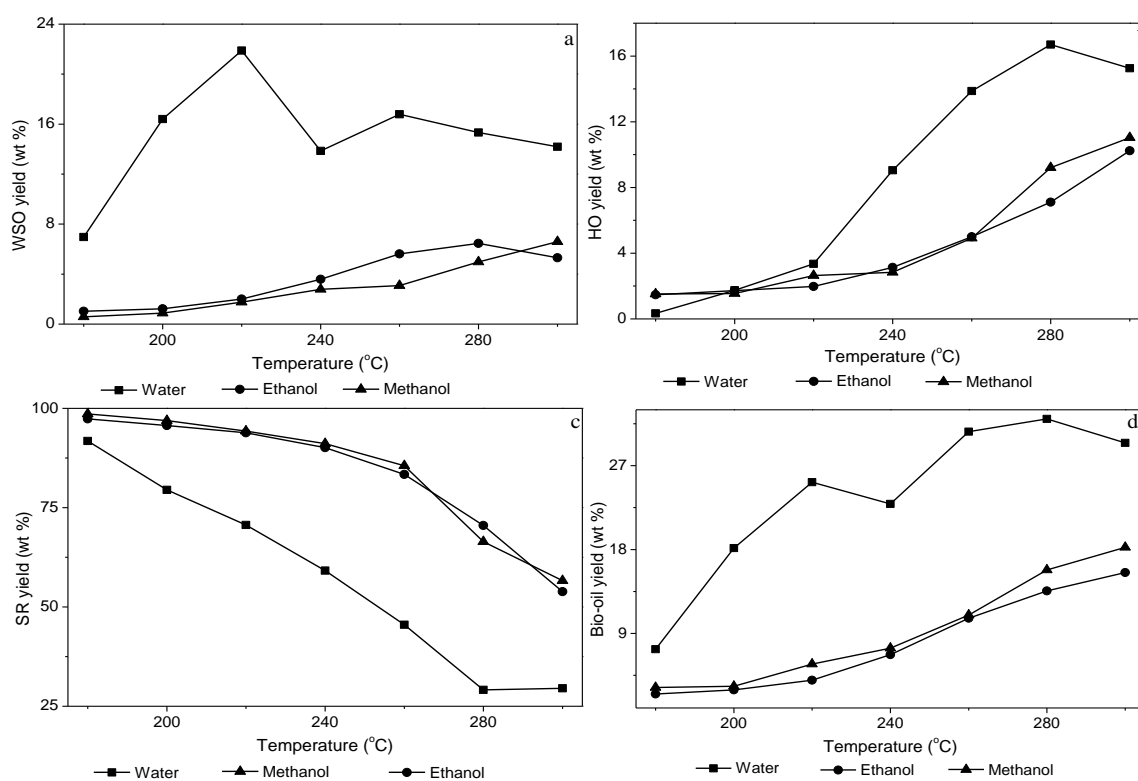


Fig. 1. Effect of solvent type on bio-oil yields at different temperatures

This result could be attributed to the following secondary reactions: (1) formation of a solid by cyclization, condensation, and re-polymerization of the bio-oil, and (2) formation of gases from degradation of the liquid products (Liu *et al.* 2008; Akhtar and Amin 2011). Increasing the temperature from 260 to 280 °C resulted in a slight increase in WSO yield from the hydrothermal liquefaction of cypress. The possible reason for this may be that water served as both reaction medium and reactant, and hot-compressed water at higher temperatures was more suitable for free radical reactions (Demirbas 2011). The conversion of free radicals to the WSO fraction was promoted in the presence of water, resulting in an increase of the WSO yield at higher temperatures. The highest bio-oil yields reached 32%, 15.5%, and 18.2% at 280, 300, and 300 °C, respectively. The bio-oil yield increased with increasing temperature for the methanol and ethanol tests.

However, the bio-oil yield increased with increasing temperature up to a certain value (280 °C) and decreased thereafter for the water tests. In the present study, water had the highest bio-oil yield; the highest yields were 21.9% and 16.7% for WSO and HO obtained at 220 and 280 °C, respectively. Consequently, considering the bio-oil yield, the solvent efficiency in the cypress liquefaction was as follows: water > methanol > ethanol.

GC-MS Analysis of Bio-Oil

The bio-oils obtained from cypress liquefaction in the three solvents were characterized by GC-MS for identification of the chemical compositions. The chemical compounds were identified using the NIST library based on the GC-MS chromatographs. The relative area% for each compound was identified as the percentage of the compound's chromatographic area with respect to the total area. Tables 1 and 2 show the possible chemical names and GC peak areas. According to the GC-MS analysis results, the bio-oils generated from cypress liquefaction in the three solvents contained phenolics, esters, aromatics, acids, furfurals, and their derivatives, but the contents and kinds of compounds were quite different from each other. In agreement with other researchers (Xu and Lad 2008), it was determined that the phenolic compounds primarily originated from the degradation of lignin in the woody biomass, and the furan and acid derivatives were formed primarily from the carbohydrate components of the biomass feedstock. Therefore, the bio-oils were divided into part A and part B, based on the origination of chemical compounds in the liquefaction process. It can be seen from Tables 1 and 2 that solvent type markedly affected the composition of the bio-oil. When using water as the liquefaction solvent, a high concentration of acidic compounds, such as 4-oxo-pentanoic acid and 4-hydroxy-3-methoxy-benzeneacetic acid, was seen. The 4-oxo-pentanoic acid was formed primarily from the conversion of cellulose and hemicelluloses *via* hydrolysis and de-polymerization reactions, and the benzeneacetic acid primarily originated from the degradation of lignin. When ethanol and methanol were used as the liquefaction solvents, the bio-oils contained a significant amount of ethyl esters and methyl esters, respectively.

Table 1. GC-MS Analysis Results for the Bio-Oils: Formation from the Decomposition of Carbohydrates (Part A)

Compound	Content (%)		
	Water	Ethanol	Methanol
Acetic acid, hydroxy-, ethyl ester		0.9	
2-Furanmethanol		1.2	
Butanoic acid, 2-hydroxy-,ethyl ester		0.4	
Ethanol, 2,2-diethoxy-		0.3	
2,5-Hexanedione	0.6		
2-Furancarboxaldehyde, 5-methyl-	0.5		
1,2-Cyclopentanedione, 3-methyl-	2.5		1.8
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-		2.6	
2-Phentanoic acid, 4-oxo-, ethyl ester		1.1	
Pentanoic acid,4-oxo-	13.4		
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-		0.9	
Furan, 2-ethoxy-2,3-dihydro-4-methyl-			2.1
2-Furancarboxaldehyde,5-(hydroxy methyl-)	8.2		
Total content	25.3	7.4	3.9

The total ethyl ester and methyl ester compound percentages were 5.1% and 14.9% in ethanol and methanol, respectively. The ester compounds' formation could be due to the esterification reaction in the liquefaction process. For example, 4-hydroxy-3-methoxy-benzeneacetic acid methyl ester was possibly produced *via* an esterification reaction between methanol and 4-hydroxy-3-methoxy-benzeneacetic acid. In contrast to ethanol and methanol, hydrothermal liquefaction products had the highest amount of carbohydrate decomposition products, such as 5-(hydroxyl methyl)-2-furancarboxaldehyde, 4-oxo-pentanoic acid, and 3-methyl-cyclopentanedione.

When ethanol and methanol were used as the solvent, the content of phenolic compounds in the bio-oil was much higher than that of the bio-oil obtained from the hydrothermal liquefaction process. In summary, the solvent could affect the formation of various compounds in the bio-oil.

Table 2. GC-MS Analysis Results for the Bio-Oils: Formation from the Decomposition of Lignin (Part B)

Compound	Content (%)		
	Water	Ethanol	Methanol
1,2-Benzenediol	3.8		4.8
Phenol, 2-methoxy-4-methyl-		4.9	2.8
Phenol, 2-methoxy-	2.2	4.1	
Benzaldehyde		0.3	0.6
Phenol			
Toluene	0.7		
1,2-Benzenediol, 3-methyl-	0.8		
Phenol, 4-ethyl-2-methoxy-	2.3		5.3
2,3-Dimethoxytoluene		6.5	
1,2-Benzenediol, 4-methyl-	0.5		
Phenol, 2-methoxy-3-(2-propenyl)-			3.6
3-Allyl-6-methoxyphenol		3.8	
Ethyl vanillin			5.5
Phenol, 2-methoxy-4-propyl		4.3	
Benzaldehyde, 3-hydroxy-4-methoxy-			2.6
4-Hydroxy-2-methoxybenzaldehyde	10.5		
Vanillin		2.1	
Phenol, 2-methoxy-4-(1-propenyl)-	1.4	10.8	17.4
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	3.5	1.6	2.9
Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester			5.7
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	6.9		5.7
Benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester		2.7	
Methyl-(2-hydroxy-3-ethoxy-benzyl)ether			6.9
Benzeneacetic acid, 4-hydroxy-3-methoxy-	13.4		
Benzenemethanol, 4-methoxy-		3.4	
Total content	46.2	44.7	64.3

Elemental Analysis of Solid Residue

The elemental compositions (C, H, O, and N) of the solid residues are shown in Table 3. The reaction temperature appears to have ultimately influenced the solid residue composition. Clearly, the carbon content increased and the oxygen content showed a downward trend as the temperature increased for all the solvent liquefaction experiments. The HHVs were calculated using Dulong's equation and increased sharply when the temperature increased from 240 to 300 °C. In fact, the HHV of biomass represented the HHV primarily from lignin and partially from cellulose and hemicelluloses. As reported in a previous paper (Demirbaş 2006), holocellulose had a HHV of 18.6 MJ/Kg, whereas lignin had a HHV of 23.3 to 26.6 MJ/Kg. Among the three components of cypress, lignin was the most difficult one to decompose, and lignin occurs in biomass primarily as lignocellulose in a complex association with cellulose (Demirbaş 2000). The HHVs of the solid residues obtained at 280 and 300 °C in water were much higher than the raw cypress and solid residues obtained at other conditions. Among the three tested solvents, water had the best effect on the HHV of solid residues at all the reaction temperatures. This result might be due to the fact that water as a reaction reactant and medium was conducive to the decomposition of cellulose and hemicelluloses *via* the hydrolysis reaction, resulting in a higher content of lignin fragments. The highest HHV of the solid residue was 26.3 MJ/Kg, similar to that of Xuzhou coal (Xiao *et al.* 2006) (23.22 MJ/Kg) and Loy yang coal (Kuchonthara *et al.* 2005) (26.4 MJ/Kg). Therefore, the higher HHV of solid residues are suitable for combustion as a solid fuel.

Table 3. Elemental Analysis of Cypress and Solid Residues Obtained at Different Temperatures

Solvents	Temperature	C (wt %)	O (wt %)	H (wt %)	O/C	HHV (MJ/Kg)
Water	240 °C	53.7	40.2	5.9	0.75	19.4
	260 °C	62.5	31.6	5.5	0.51	23.4
	280 °C	69.4	25.2	5.0	0.36	26.2
	300 °C	70.1	24.7	4.9	0.35	26.3
Ethanol	240 °C	51.0	42.6	6.1	0.84	18.4
	260 °C	51.8	41.7	6.1	0.80	18.9
	280 °C	54.3	39.4	6.0	0.72	19.9
	300 °C	58.4	35.5	5.7	0.61	21.6
Methanol	240 °C	50.7	43.0	6.1	0.85	18.1
	260 °C	51.4	42.3	6.0	0.82	18.5
	280 °C	54.3	39.5	5.9	0.73	19.7
	300 °C	57.1	36.8	5.8	0.64	21.0

Sugar Analysis of Solid Residue

To investigate the structural features of the raw cypress and solid residues obtained from different reaction conditions, their sugar components were identified and qualified by analysis of the sugars obtained with the sulfuric acid hydrolysis method; the results are presented in Fig. 2. The primary sugars of the raw cypress were glucose (mainly from cellulose), which accounted for about 21.3% of the sample, followed by mannose (from hemicelluloses), which accounted for 11.8%. Additionally, small amounts of xylose (4.5%), galactose (1.4%), and arabinose (0.59%) were also present. From Fig. 2, it is clear that the sugar ratio of the residue strongly depended on the solvent in the temperature range of 180 to 300 °C.

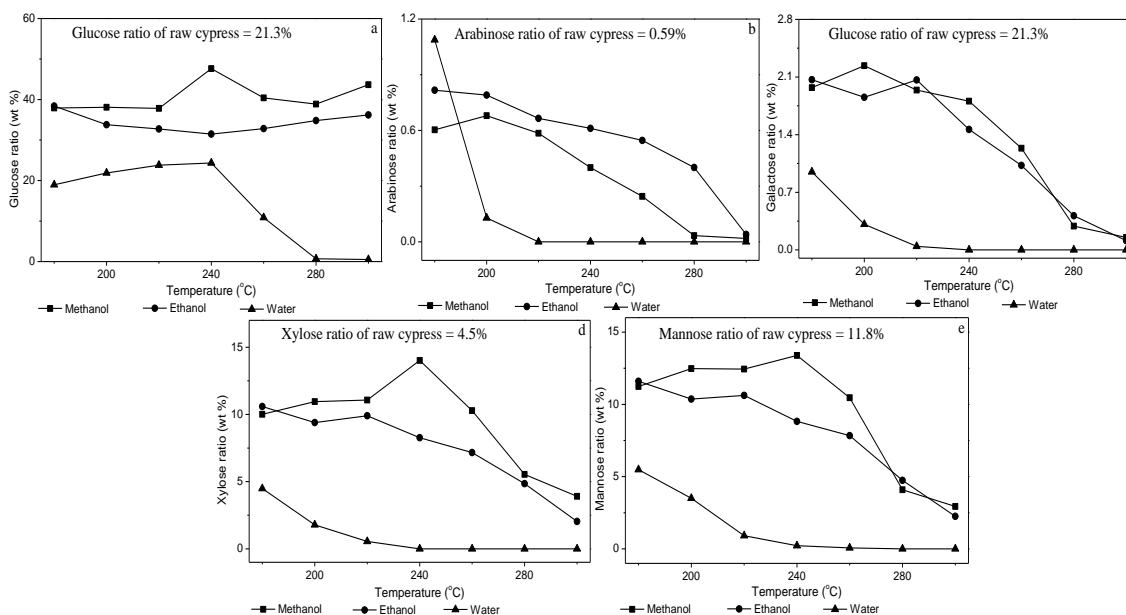


Fig. 2. Sugar analysis of solid residues at different reaction conditions (A-glucose ratio, B-arabinose ratio, C-galactose ratio, D-xylose ratio, and E-mannose ratio)

The glucose ratio of the residue obtained from hydrothermal cypress liquefaction increased with increasing reaction temperature at first, followed by a rapid decrease with further increasing reaction temperature. This was due to the decomposition of hemicelluloses (mannose, xylose, galactose, and arabinose) at lower temperatures (see Fig. 2). Conversely, the xylose and mannose ratios in the residue obtained from cypress liquefaction in methanol increased at lower temperatures (180 to 240 °C), and then decreased with increasing temperature. This might be due to lignin being dissolved first and then separated from cypress at operating temperatures of 180 to 240 °C in the presence of methanol. The result showed that cellulose and hemicelluloses in cypress did not dissolve in methanol at lower temperatures. As shown in Fig. 2, the residues from the methanol showed a higher ratio compared to that of water and ethanol. With respect to the sugar ratio in residues from the three tested solvents, water had the best effect on the decomposition of carbohydrates (cellulose and hemicelluloses).

FT-IR Analysis

Figure 3 shows the FT-IR spectra of raw cypress and solid residues after liquefaction with the three tested solvents. Woody biomass is composed of cellulose, hemicelluloses, and lignin. According to the literature (Liu *et al.* 2008; Sun *et al.* 2011), the bands in the spectra of raw cypress and solid residues can be assigned as follows. The band at 3362 cm^{-1} was caused by -OH (stretching vibration) in cypress and water. Xylans of hemicelluloses have characteristic absorption at 1722 cm^{-1} (C=O stretching vibration, carbonyl, and ester groups). Cellulose has its characteristic absorption peaks at about 3362, 2900 (-CH₃, -CH₂ stretching), 1365 (-CH₃ bending vibration), and 1143 cm^{-1} (C-H stretching vibration). The spectrum of lignin shows some distinct bands, with absorption at 2900, 1600 to 1500 (aromatic skeletal C=C stretching vibration), 1416 (-CH₂ bending vibration), 1314 (O-H in-plane bending vibration), and 830 to 750 cm^{-1} (aromatic ring). The band at 1700 cm^{-1} almost disappeared after liquefaction at 260 °C, showing that hemicellulose decomposition preceded that of cellulose and lignin in all tested solvents.

The effect of solvent type on cypress liquefaction can be clearly seen from the cellulose and lignin decompositions. As can be seen in Fig. 3, water, rather than methanol or ethanol, gave priority to the cellulose decomposition at 280 °C, and this was confirmed by the disappearance of bands at 1365 cm^{-1} . A relatively higher content of cellulose can be confirmed by the high intensity of the band at 1365 cm^{-1} when ethanol and methanol were solvents after liquefaction at 280 °C. The weak absorption at 830 and 1600 cm^{-1} implied the presence of lignin fragments in the solid residue obtained from the liquefaction of cypress in all tested solvents at 300 °C. Therefore, the decomposition velocities of cellulose, hemicelluloses, and lignin were different in all the tested solvents.

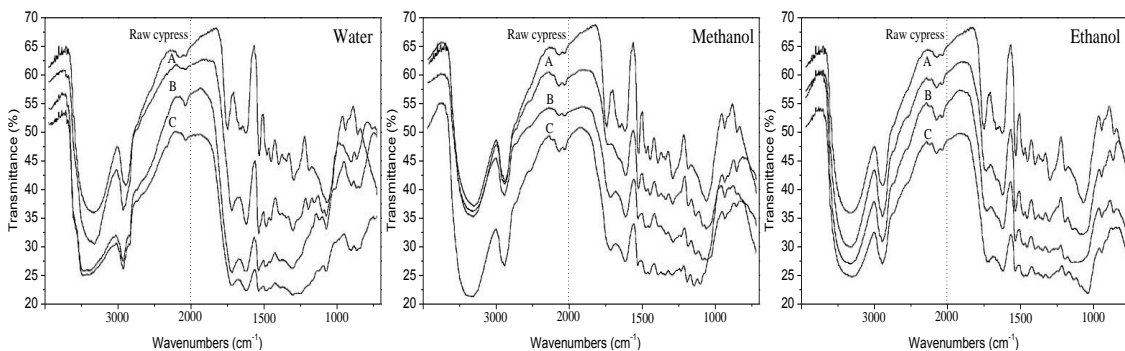


Fig. 3. FT-IR analysis of raw cypress and solid residues (A – 260 °C, B – 280 °C, C – 300 °C)

CONCLUSIONS

1. The solvent could affect the formation of various compounds in the bio-oil. Considering the bio-oil yield, the solvent efficiency in the cypress liquefaction was as follows: water > methanol > ethanol.
2. Water had the most pronounced effect on the decomposition of carbohydrates and the HHV of residues.
3. The decomposition velocities of cellulose, hemicelluloses, and lignin were different in all solvents. Hemicellulose decomposition preceded cellulose and lignin in all solvents.

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