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Mechanisms and Main Regularities of Biomass Liquefaction with Alcoholic Solvents

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The effects of three alcoholic solvents, including monohydric *n*-octanol, dihydric ethylene glycol, and trihydric glycerol, on the process of biomass liquefaction were studied by thermogravimetry (TG) analysis. The results showed that there were three stages during biomass liquefaction, including biomass dehydration, volatilization of alcoholic solvents, and biomass alcoholysis. At the stage of biomass alcoholysis, alcoholic solvents combined with fragments from biomass cracking, which resulted in exothermic reaction and formed lowly volatile compounds. The reaction temperature T_R of biomass alcoholysis increased in the following order: T_R (*n*-octanol + biomass) < T_R (ethylene glycol + biomass) < T_R (glycerol + biomass). In addition, the effects of these alcoholic solvents on the product distributions and liquefaction yields have also been investigated with a stainless-steel autoclave. The results indicated that *n*-octanol was the best solvent for biomass liquefaction. The highest liquefaction yield of 83.54 wt % was obtained with *n*-octanol; meanwhile, the content of net light oil was up to 30 wt %, and the content of unreactive *n*-octanol reached 55.62 wt %. Moreover, the gas chromatography–mass spectrometry (GC–MS) results suggested that only five organic compounds, including acetic-octyl-ester, hexanoic-4-octyl-ester, 5-methyl-furfural, octyl-ether, and unreactive *n*-octanol, have been found in the light oil. The simple components of light oil were beneficial to the separation of valuable chemicals and recycle of unreactive *n*-octanol. Although ethylene glycol and glycerol can also promote the cracking of biomass, a single molecule of polyhydric alcohol can be combined with multimolecular cracking fragments. Consequently, the liquefaction yields of biomass were less than 60 wt %, and the main products were heavy oil and residue.

1. Introduction

Traditional liquefaction processes, such as the hydrothermal upgrading (HTU) process, are normally performed under high temperature and high pressure.^{1,2} The products from the complex and expensive processes are complex mixtures and very difficult to separate into certain pure chemicals.^{3–5} To produce superior quality light species from biomass under milder conditions, it is essential to develop economical and energy-efficient liquefaction processes. Previous studies have shown that solvent type significantly affects the yield and composition of products during biomass liquefaction processes.^{6–8} Among those studies, alcoholic solvents have attracted considerable attention because of their obvious

reactive activity.^{9–11} Yamazaki et al.¹² studied the liquefaction of beech wood in various supercritical alcohols without any catalysts and found that more than 90% wood was decomposed and liquefied in all alcohols under 350 °C for only 3 min. Alcohols with longer alkyl chains liquefied biomass in shorter reaction times. Demirbas et al.¹³ investigated the conversion of biomass in anhydrous glycerin in the presence of Na₂CO₃ and KOH and found that the most significant factors were those of the maximum temperature, reaction time, and amount of alkali. Although alkaline solutions promoted the depolymerization of biomass, they also increased the temperature of depolymerization. Rezzoug et al.^{14,15} assessed the liquefaction of milled wood in acidified ethylene glycol and found that, even if the temperature decreased to 250 °C, the liquefied wood yield was still above 80% when adding 1.5% H₂SO₄ as a catalyst.

Although alcoholic solvents have shown obvious reactive activity in many works, it is still unclear how alcoholic solvents affect the biomass liquefaction process. To produce superior quality light species from biomass, it is necessary to understand the mechanisms of biomass liquefaction with alcoholic solvents. In this paper, the effects of three alcoholic solvents, including monohydric alcohol (*n*-octanol) and polyhydric alcohols (ethylene glycol and glycerol), on the biomass liquefaction process were examined by thermogravimetry (TG) analysis. In addition, the product distributions and liquefaction

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yields were also investigated with a stainless-steel autoclave. Furthermore, the characterizations of liquefied products were carried out by a gas chromatograph equipped with a mass selective detector (GC–MS) and Fourier transform infrared spectroscopy (FTIR) to probe liquefaction mechanisms of biomass with alcoholic solvents and study the feasibility of separation of valuable chemicals and recycle of unreactive alcoholic solvents.

Table 1. Chemical and Elemental Compositions of Biomass Samples (wt % on a Dry Basis)

chemical composition	content (wt %)	elemental composition	content (wt %)
lignin	21.38	C	47.02
hemicellulose	31.37	H	6.01
α -cellulose	45.33	O ^a	46.76
ethanol–benzene solubles	4.45	N	0.21
cold water solubles	3.36		
ash	0.54		

^a By difference.

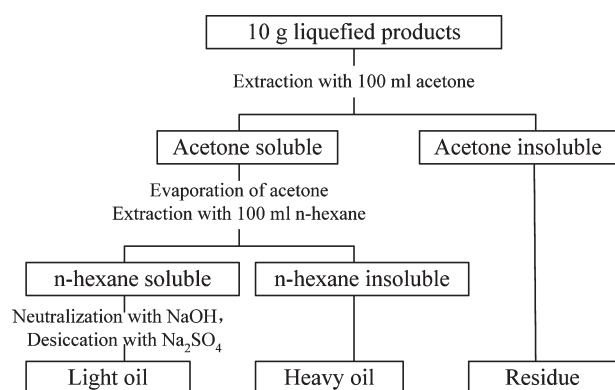


Figure 1. Procedure for liquefied product separation.

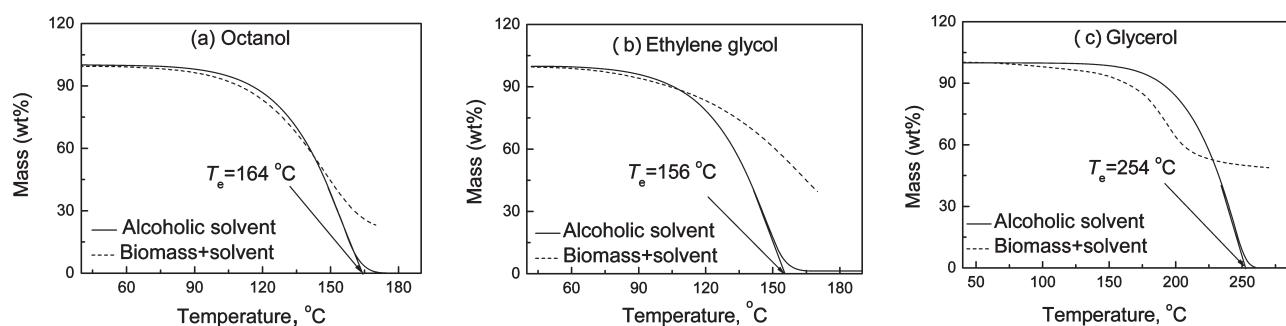


Figure 2. TG curves of the liquefaction process of biomass with alcoholic solvents.

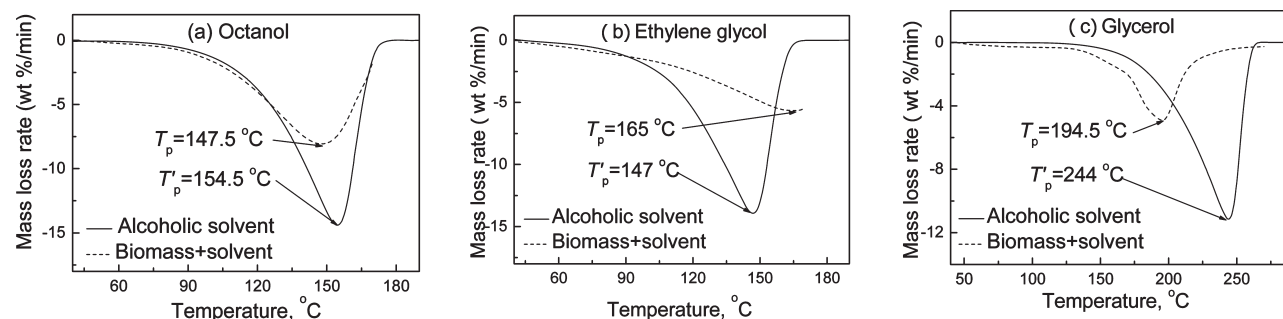


Figure 3. DTG curves of the liquefaction process of biomass with alcoholic solvents.

2. Experimental Section

2.1. Biomass Samples and Alcoholic Solvents. The applied biomass samples are poplar from the suburb of Beijing, China. Biomass samples were first ground and sieved. Only the fraction retained between 0.18 and 0.9 mm sieve was used. The biomass powder samples were dried at 105 °C for 12 h before they were used. Their chemical and elemental compositions are listed in Table 1.

Three alcoholic solvents, including monohydric *n*-octanol (boiling point 194–195 °C), dihydric ethylene glycol (boiling point 197.6 °C), and trihydric glycerol (boiling point 290 °C) were acidified by premixing with 3 wt % sulfuric acid, respectively. All alcoholic solvents used were analytical reagent-grade and obtained from commercial sources.

2.2. Experimental Procedure. The TG analyzer (Netzsch STA449) was used to study the liquefaction process of biomass with alcoholic solvents. The mass of biomass samples was approximately 5 ± 0.5 mg, and the mass of acidified alcoholic solvents was 2-fold of that of biomass samples. All of the TG tests were carried out in a temperature range from 40 °C to the setting temperature, which was 20 °C lower than the boiling point of pure alcoholic solvents at a heating rate of 30 °C/min. The carrying gas in all TG test runs was high-purity N₂ controlled at a constant flow rate of 80 mL/min. Moreover, the blank control experiments of pure alcoholic solvents were also carried out in the same TG analyzer.

To study the product distributions and liquefaction yields, a set of experiments was carried out in a 2 L stainless-steel autoclave (TAS-2, Taiatsu Techno Co.). In a typical run, 178.5 g of biomass samples were placed in the autoclave together with 2-fold acidified alcoholic solvents. The air in the autoclave was replaced by N₂. The autoclave was heated and controlled at the peak temperature T_R of DSC curves of biomass liquefaction for 60 min [T_R (*n*-octanol + biomass) = 143.5 °C; T_R (ethylene glycol + biomass) = 160 °C; T_R (glycerol + biomass) = 191 °C]. With the temperature increasing from room temperature to T_R , the pressure P in the autoclave increased from ambient pressure to 0.4–1.2 MPa [P (*n*-octanol + biomass) = 0.5 MPa; P (ethylene glycol + biomass) = 0.4 MPa; P (glycerol + biomass) = 1.2 MPa]. After reaction, the autoclave was cooled to room temperature by air and the pressure automatically decreased to ambient pressure. Therefore, the

gaseous products were vented because the yield of gaseous products was almost negligible. The solid and liquid products were poured into a beaker.

2.3. Separation of Liquefied Products. A total of 10 g liquefied products was filtered in a 30 mL crucible with a medium fit (number 4). During filtration, 100 mL of acetone was used for washing solid products. After filtration, the solid products was dried at 105 °C for 12 h, then weighed, and designated as residue. Upon removal of the acetone under reduced pressure in a rotary evaporator, this acetone-soluble fraction was extracted with 100 mL of *n*-hexane. The *n*-hexane-insoluble fraction was dried at 80 °C for 12 h under vacuum, then weighed, and called heavy oil. The *n*-hexane solution was neutralized with NaOH (1.5 N), dried over anhydrous sodium sulfate, filtered, and evaporated in a rotary evaporator. This fraction was weighed and designated as light oil. During the reproducibility of the experimental runs, a $\pm 3.0\%$ standard deviation was observed for the mass of residue, heavy oil, and light oil.

2.4. Characterization of Liquefied Products. The light oil was analyzed qualitatively by GC–MS [HP6890/5972; column, HP-1; cross-linked methyl siloxane, 25 m \times 0.32 mm \times 0.17 μ m; temperature program, 40 °C (hold for 10 min) \rightarrow 300 °C (rate 5 °C/min) hold for 10 min]. Because of the good solubility of *n*-hexane, all of unreactive alcoholic solvents remained in light oil. The content of unreactive alcoholic solvents in light oil was determined by an external standard method. The content of net light oil without alcoholic solvents is calculated by the normalization method. The residue and heavy oil products were analyzed by a FTIR spectrometer (Bruker Equinox55), which was operated with 32 scans at a resolution of 4 cm^{-1} and applied at a wavenumber range from 4000 to 400 cm^{-1} .

3. Results and Discussion

3.1. Thermal Analysis of the Liquefaction Process of Biomass with Alcoholic Solvents. The abscissa temperature of the

Table 2. Basic Thermal Chemistry Data of Samples from TG, DTG, and DSC Curves

sample	weight loss (wt %)	residue rate ϕ (wt %, biomass basic)	T_p (°C)	T_R (°C)
<i>n</i> -octanol + biomass	73.30	0.801	147.5	143.5
ethylene glycol + biomass	45.08	1.650	165	160
glycerol + biomass	50.18	1.495	194.5	191

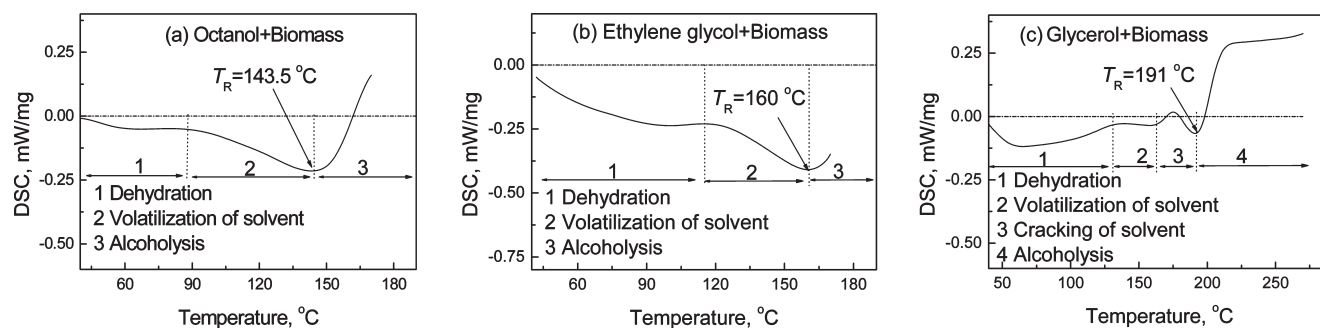


Figure 4. DSC curves of the liquefaction process of biomass with alcoholic solvents.

Table 3. Product Distributions and Liquefaction Yields during Biomass Liquefaction

samples	content of liquefied products (wt %)				liquefaction yield η (wt %, biomass basic)
	unreactive solvents	net light oil ^a	heavy oil	residue	
<i>n</i> -octanol + biomass	55.62	27.98	11.02	5.38	83.54
ethylene glycol + biomass	43.31	0.57	41.16	14.96	54.22
glycerol + biomass	27.00	4.14	55.1	13.77	57.86

^a By difference.

tangent to the TG curves of pure alcoholic solvents is designed as the end temperature T_e of volatilization of alcoholic solvents. Figure 2 shows the effects of alcoholic solvents on the weight loss during the biomass liquefaction process from room temperature to the end temperature T_e . The variation of the rate of weight loss with temperature is shown in Figure 3.

As shown in Figures 2 and 3, the rate of weight loss of biomass-mixed solvents is higher than that of volatilization of pure alcoholic solvents at low temperature because of the desorption of the adsorbed moisture and volatile compounds in biomass samples. However, the maximum weight loss rate

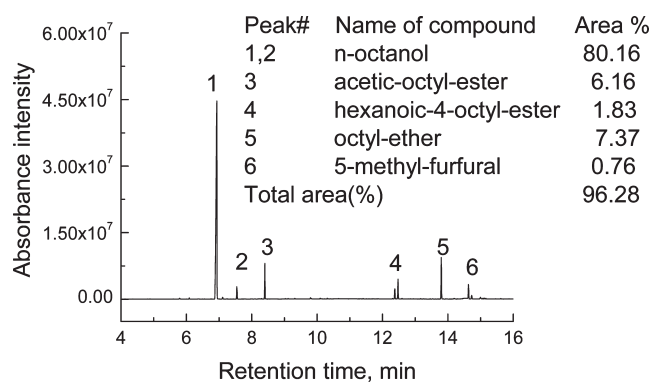


Figure 5. GC–MS analysis on light oil from biomass liquefaction with *n*-octanol.

Table 4. Band Assignment for FTIR Spectra of Functional Groups

wavenumber (cm^{-1})	assignment of functional group
3700–3200	–OH stretching
3000–2800	C–H stretching
1730	carbonyl C=O stretching
1600, 1500	aromatic rings stretching
1470–1430	C–O stretching in O–CH ₃
1234	C–O–C stretching in alkyl aromatic
1157	C–O–C asymmetry stretching
1057	C–O stretching
1033	C–O stretching in O–CH ₃
900–700	C–H stretching

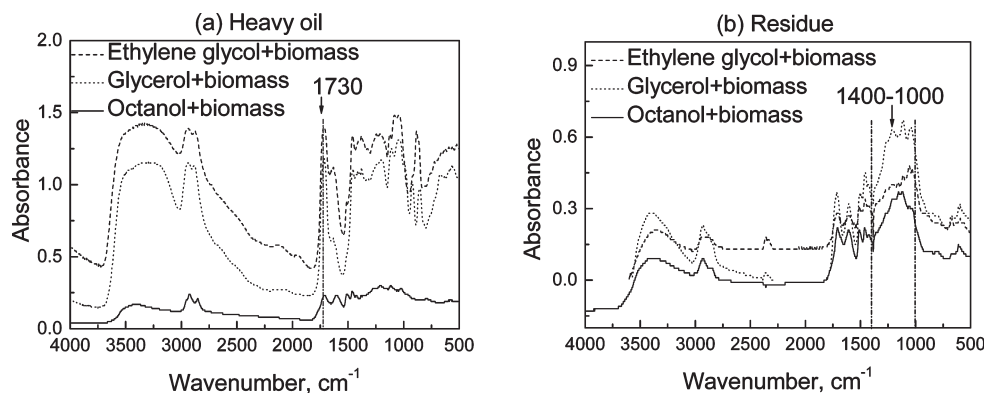


Figure 6. FTIR spectra of heavy oils and residue from biomass liquefaction with alcoholic solvents.

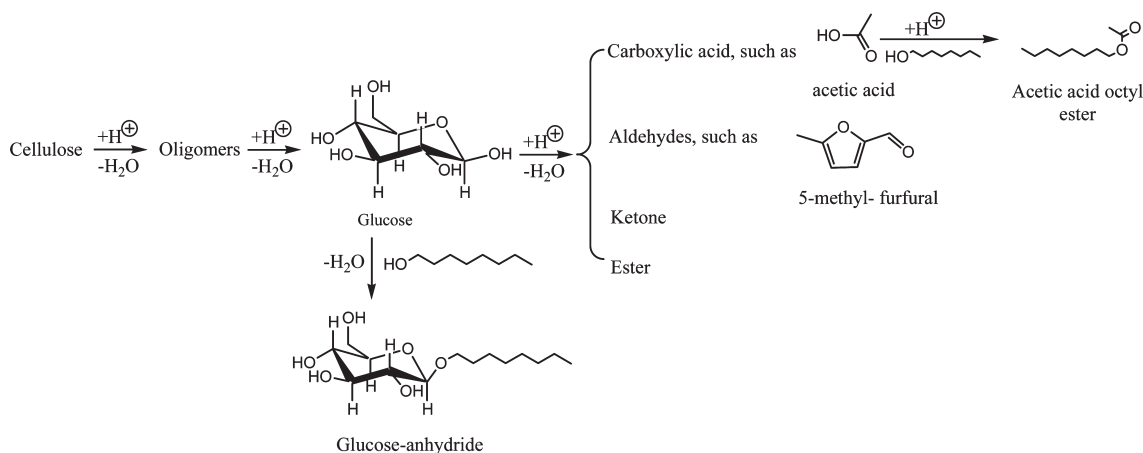


Figure 7. Cellulose alcoholysis pathways catalyzed by acid.⁴

$-(dW/dt)_{\max}$ of biomass-mixed solvents is lower than that of pure alcoholic solvents. As a result, some residue still remains in the TG analyzer when volatilization of pure alcoholic solvents is over. At the end temperature T_e , the residue rate ϕ can be calculated with the following formula:

$$\phi = \frac{\text{mass of residue in TG analyzer at } T_e}{\text{mass of initial dry biomass samples}} \times 100\% \quad (1)$$

Table 2 shows the residue rate ϕ . It can be seen that the residue rate presents the following increasing order:

$$\phi_{(n\text{-octanol} + \text{biomass})} < \phi_{(\text{glycerol} + \text{biomass})} < \phi_{(\text{ethylene glycol} + \text{biomass})}$$

Furthermore, the mass of residue from biomass liquefaction with glycerol and ethylene glycol is 1.495–1.650 times as much as that of initial biomass at the end temperature T_e . This result indicates that, in alcoholic solvent, some molecular or functional groups of biomass are likely to be alcoholized to form new molecules and to facilitate the liquefaction of biomass.

3.2. Analysis of the Enthalpy of the Liquefaction Process of Biomass with Alcoholic Solvents. The DSC curves showing energy consumption property during the liquefaction process of biomass with alcoholic solvents were also measured. The results are plotted in Figure 4. Obviously, at the first stage 1 and 2, the reaction is endothermic, mainly attributed to the removal of moisture and volatilization of solvent, respectively. With temperature increasing further, the DSC values of biomass alcoholysis with *n*-octanol and glycerol increase and become positive, which means that biomass alcoholysis is an exothermic reaction. Furthermore, it can be

found that the peak temperature T_R of DSC curves is lower than the peak temperature T_p of DTG curves during biomass alcoholysis with the three alcoholic solvents (shown in Table 2). This result indicates that the rate of weight loss of biomass samples still increases with the temperature increasing from T_R to T_p . However, the total endothermic caloric of biomass cracking and solvents volatilization is lower than the exothermic caloric of biomass alcoholysis. As a result, the global liquefaction process is exothermic. The temperature of biomass alcoholysis shows the following increasing order:

$$T_R (n\text{-octanol} + \text{biomass}) < T_R (\text{ethylene glycol} + \text{biomass}) < T_R (\text{glycerol} + \text{biomass})$$

3.3. Effect of Alcoholic Solvents on the Product Distributions and Liquefaction Yields. The liquefaction yield η is given by the ratio

$$\eta = \left(1 - \frac{\text{mass of residue in autoclave}}{\text{mass of initial dry biomass}}\right) \times 100\% \quad (2)$$

Table 3 shows that the highest liquefaction yield of 83.54 wt % was obtained with *n*-octanol but that the liquefaction yields of biomass with polyhydric alcoholic solvents were less than 60 wt %. This result suggests that biomass cracks more easily in monohydric *n*-octanol than in polyhydric alcohols.

The fraction distributions of the liquefied product are also given in Table 3, which indicates that the content of net light oil from biomass liquefaction with *n*-octanol is up to 30 wt %

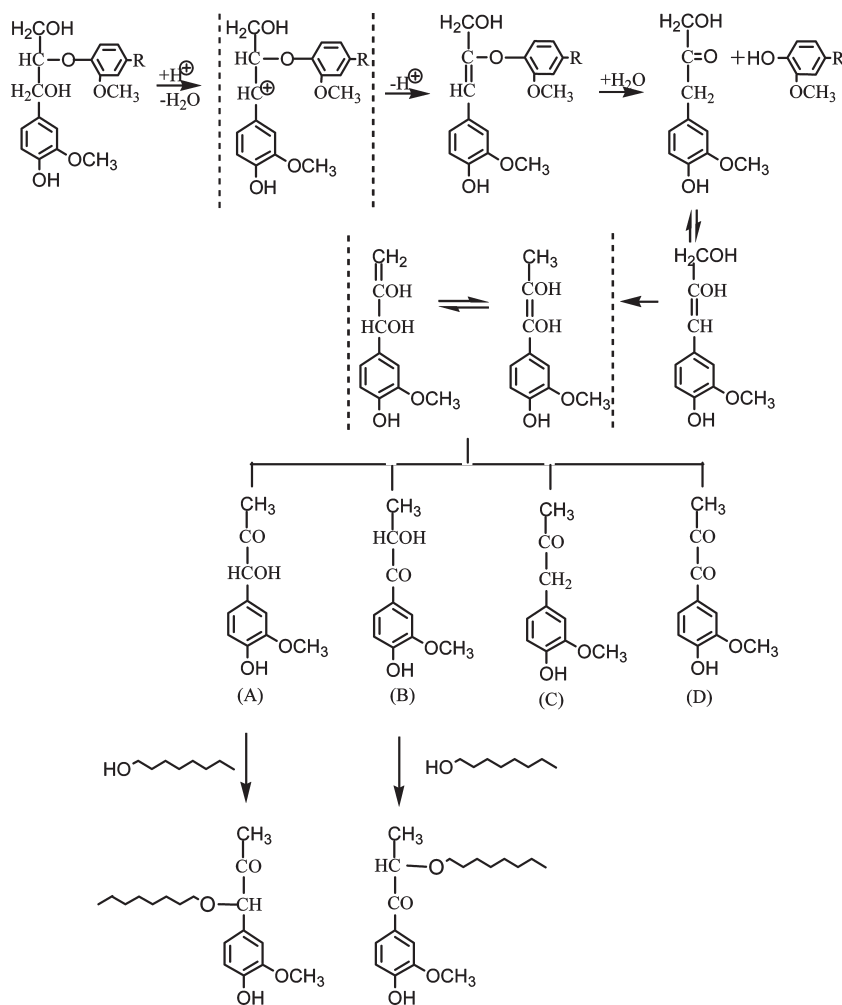


Figure 8. Lignin alcoholysis pathways catalyzed by acid.²¹

and the content of unreactive *n*-octanol reaches 55.62 wt %. Both contents are all highest among the same type of contents. However, the contents of net light oil from biomass liquefaction with polyhydric alcoholic solvents are almost negligible when compared to those of the heavy oil and residue. This result indicates that condensation and polymerization reactions take place among some parts of depolymerized and degraded compounds from biomass liquefaction with polyhydric alcoholic solvents.

3.4. Characterizations of Products from Biomass Liquefaction. GC–MS analysis of the light oil from biomass liquefaction with *n*-octanol is presented in Figure 5. The results of chromatographic areas (percentage of total area) belong to the identified compounds. The difference to 100% area represents the area of unidentified compounds. It can be seen from Figure 5 that only five main compounds, including unreactive *n*-octanol, acetic-octyl-ester, hexanoic-4-octyl-ester, octyl-ether, and 5-methyl-furfural, are observed in the light oil from biomass liquefaction with *n*-octanol. This result suggests that monohydric *n*-octanol promoted directionally cellulose and hemicellulose to crack into organic acids and aldehydes and reacted further with organic acids to form esters. In comparison to more than 400 organic compounds found in conventional bio-oils, the components of light oil from biomass liquefaction with *n*-octanol are simple and highly concentrated.⁴ These specialties of light oil are useful to separate valuable chemicals and recycle unreactive *n*-octanol.

Figure 6 gives the FTIR spectra of the heavy oils and residue. The infrared absorption band assignment of the functional groups of heavy oils and residue is shown in Table 4.^{16–19} As shown in Figure 6 and Table 4, the FTIR spectra of heavy oils and residue include the stretching vibration of hydroxyl groups (3500–3200 cm^{−1}), stretching vibration of carbonyl groups (1850–1650 cm^{−1}), stretching vibration of the aromatic ring (1600 and 1500 cm^{−1}), and stretching vibration of aether groups (1400–1000 cm^{−1}). The hydroxyl groups mainly originate from alcoholic solvents, and carbonyl groups and aromatic groups might be from the degradation products of cellulose, hemicellulose, and lignin.^{17,18} Moreover, the aether groups might be not only from the biomass fragments but also from the dehydration and condensation products between the biomass fragments and alcoholic solvents.

The results of FTIR analysis presented in Figure 6a indicate that the bands of carbonyl groups (1730 cm^{−1}) in heavy oils from biomass alcoholysis with polyhydric alcoholic solvents are relatively stronger than those with *n*-octanol. This result suggests that more molecular fragments can be combined with

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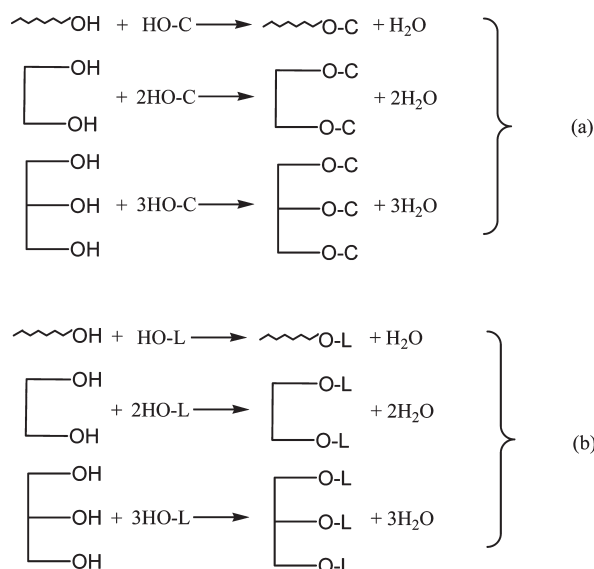


Figure 9. Mechanisms of alcoholic solvents combine with fragments from biomass liquefaction.

polyhydric solvents during biomass alcoholysis. Furthermore, the bands of ether groups ($1400\text{--}1000\text{ cm}^{-1}$) in residue are relatively stronger than those in heavy oils, which suggest that the ether groups between fragments and alcoholic solvents can be further improved after dehydration and condensation reactions.²⁰

3.5. Mechanisms of Biomass Liquefaction with Alcoholic Solvents. It is well-known that cellulose, hemicellulose, and lignin are the three main components of biomass. These components can be alcoholized with acid as a catalyst according to the pathways shown in Figures 7 and 8, respectively.^{4,21} The intermediates include glucose and xylose from cellulose and hemicellulose degradations, denoted as C-OH, and also include the fragments A and B from lignin degradation, designed as L-OH. These intermediates can react further with alcoholic solvents according to the mechanisms proposed

in Figure 9. In the presence of monohydric *n*-octanol, a single molecule of *n*-octanol can be only combined with one C-OH or L-OH. However, when using ethylene glycol or glycerol, a single molecule of polyhydric alcohol can be combined with multimolecular C-OH or L-OH. As a result, the molecular weight of products is increased and the formation of heavy oil and residue is promoted with polyhydric alcohols.

3. Conclusions

(1) There are three stages during biomass liquefaction with alcoholic solvents, including biomass dehydration, volatilization of alcoholic solvents, and biomass alcoholysis. At the stage of biomass alcoholysis, alcoholic solvents are combined with fragments from biomass cracking, which results in exothermic reaction and forms lowly volatile compounds. The reaction temperature T_R of biomass alcoholysis shows the following increasing order: T_R (*n*-octanol + biomass) < T_R (ethylene glycol + biomass) < T_R (glycerol + biomass). (2) Among the three alcoholic solvents, the liquefaction efficiency of *n*-octanol is the highest. The highest liquefaction yield of 83.54 wt % is obtained with *n*-octanol; meanwhile, the content of net light oil is up to 30 wt %, and the content of unreactive *n*-octanol reaches 55.62 wt %. On the contrary, when using ethylene glycol or glycerol as liquefaction solvents, the liquefaction yields of biomass are less than 60 wt % and the main products are heavy oil and residue. (3) Only five compounds including unreactive *n*-octanol, acetic-octyl-ester, hexanoic-4-octyl-ester, octyl-ether, and 5-methyl-furfural, are observed in the light oil from biomass liquefaction with *n*-octanol. The simple components of light oil are useful to separate valuable chemicals and recycle unreactive *n*-octanol. (4) A single molecule of *n*-octanol can be only combined with one C-OH or L-OH. However, when using ethylene glycol or glycerol, a single molecule of polyhydric alcohol can be connected with multimolecular C-OH or L-OH. As a result, the molecular weight of products is increased and the formation of heavy oil and residue is promoted with polyhydric alcohols.

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