



# Liquefaction of fermentation residue of reed- and corn stover-pretreated with liquid hot water in the presence of ethanol with aluminum chloride as the catalyst



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## HIGHLIGHTS

- Aluminum chloride significantly promotes liquefaction process of fermentation residues.
- Process conditions of liquefaction with aluminum chloride were optimized.
- The products and residues after liquefaction were identified in detail.

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## ABSTRACT

Bioethanol fermentation residues of reed- and corn stover-pretreated with liquid hot water were liquefied using aluminum chloride as the main catalyst in the presence of ethanol. Effects of various liquefaction conditions on the liquefied residue content were investigated. Compositions of the liquefaction products were analyzed after being separated into three fractions: water-insoluble fraction, chloroform extract, and remaining product after chloroform extraction. The major component of water-insoluble fraction was lignin. After chloroform extraction, the extracted fractions were mainly esters, phenols, hydrocarbons, and their derivatives, and the residues mainly contained some acids such as levulinic acid, acetic acid, propionic acid and formic acid. It was found that aluminum chloride promoted the liquefaction process significantly in the presence of ethanol, and breakdown of some linkage bonds in lignin of the fermentation residues, such as methoxy group, C–C and C–O, was occurred in the liquefaction process.

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## 1. Introduction

Increasing interest has been given on the conversion of lignocellulosic biomass to liquid fuels because of the limited amount of fossil fuels available, its increasing price, the need for national energy independence, and safety [1]. Lignocellulosic biomass is the most abundant renewable resource in the world; it can be converted to useful bio-ethanol by three stages: pretreatment, enzymatic hydrolysis, and fermentation. After fermentation, a large number of fermentation residues are produced. The utilization of these fermentation residues has become an attractive

prospect as it avoids the waste of resources and environmental pollution. These fermentation residues include a large number of biomass that can provide more usable energy and less pollution. Liquefaction is a very effective method to convert those fermentation residues into liquid products [2]. Liquefaction is the thermal degradation of lignocelluloses and other organic materials in a solvent under intermediate temperature and high pressure conditions [3–5]. The advantage of liquefaction is that the bio-fuel produced by liquefaction is not miscible with water, has lower oxygen content, and consequently has higher energy content. Results of previous biomass liquefaction research have been reviewed by several different authors [6–8]. The overall objective of biomass liquefaction is to control the reaction process, using pressure and/or catalysts, to produce biofuels. Notably, the solvent is a critical factor for improving the yield of the liquefied products during the liquefaction process. Multi-hydroxy compounds are well known liquefaction solvents for biomass

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liquefaction [9]. Alcohol is a class of substances that are typically used as liquefaction solvent and includes methanol [10,11], ethanol [12], ethylene glycol [13], polyethyleneglycol [13,14], glycerol [15], 2-propanol [16], 2-butanol [1], and so on. Ethanol appears more promising for biomass liquefaction as it is effective for liquefaction and is also a renewable source that can be produced from the bio-conversion of lignocellulosic biomass [12]. In recent years, studies on the liquefaction of lignocellulosic biomass in the presence of ethanol have been reported [9,17–20]. To improve the liquefaction reaction, some catalysts were used in the liquefaction of lignocellulosic biomass, such as HCl [21], H<sub>2</sub>SO<sub>4</sub> [22], FeS [23], NaOH [24], Na<sub>2</sub>CO<sub>3</sub> [24], K<sub>2</sub>CO<sub>3</sub> [25], KOH [26], and solid super-acid SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [1], solid alkali CaO-ZrO<sub>2</sub> [1], Rb<sub>2</sub>CO<sub>3</sub>, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O [27], and so on. Sulfuric acid is most often used to promote an efficient liquefaction process. In a previous study, the use of sulfuric acid as a catalyst in liquefaction promoted the degradation in the earlier stage and also the re-condensation of fragments in the later stage [28]. Another research showed that lignin fragments were more suitable to re-condense in an acid medium [29]. In our study, the fermentation residue contained more lignin and less cellulose and hemicellulose than other biomasses, which may affect the liquefaction reaction. Thus, the selection of a suitable catalyst is very important. Our preliminary investigation found that aluminum chloride as catalyst promoted the cleavage of lignin in black liquor during the heating treatment process of black liquor from alkaline pulping industry. Meanwhile, the reaction temperature and pressure also decreased [30]. Based on the results, we speculate that the aluminum chloride may be beneficial to the liquefaction of lignocellulosic biomass, but the use of aluminum chloride as a catalyst in the process of liquefaction reaction of lignocellulosic biomass has not been reported. In this work, aluminum chloride was adopted for the improvement of the liquefaction process. The liquefaction reactions of the bioethanol fermentation residues of reed- and corn stover-pretreated with liquid hot water in the presence of ethanol, using aluminum chloride as the catalyst, were investigated. The liquefaction reactions were optimized using the following treatment variables: liquefaction temperature, liquefaction reaction time, and aluminum chloride loading. Compositions of the liquefaction products were analyzed after being separated into three fractions: water-insoluble fraction, chloroform extract, and remaining product after chloroform extraction.

## 2. Materials and methods

### 2.1. Materials

Reed was provided by the Yingkou papermaking mill, Yingkou, Liaoning Province, China. Corn stover was collected from a field near Jinzhou New District, Dalian, China. The chemical compositions of reed and corn stover were determined and are shown in Table 1. The reed and corn stover were pretreated with liquid hot water at 210 °C for 20 min. The water-insoluble solids after liquid hot water pretreatment were fermented to produce ethanol. The fermentation residues were collected and milled to

a particle size of 100-mesh using a laboratory ball mill (Taijihuan Nanometer Limited Company, Qinhuangdao, China). The milled fermentation residues were dried at 105 °C for 24 h, stored in a sealed plastic bag, and placed in a desiccator until used in the liquefaction experiments.

### 2.2. Liquefaction reaction process

One gram of the milled fermentation residue was placed in a 25 mL stainless-steel tank. The loaded catalyst (anhydrous aluminum chloride) was calculated by weight content (%) based on the amount of the milled fermentation residues. Anhydrous ethanol of 20 mL volume was also placed into the tank. After shaking, the tank was placed in a blast electric oven at 100 °C, heated to 210–260 °C, and kept at that temperature for 1–4 h. By the end of liquefaction, the tank was immersed in cold water to end the reaction as fast as possible. The reaction mixture was separated by centrifugation into the liquefied product fraction and the liquefied residue fraction using a low-speed centrifuge (Beijing Lab centrifuge Limited Company, Beijing, China) with a rotating speed of 4000 rpm for 10 min. The liquefied product was collected in bottles for follow-up analysis. The liquefied residue was repeatedly washed with 1,4-dioxane, dried at 105 °C to constant weight, and weighed for content. Each experiment was performed using three parallel samples and the standard error was calculated using Microsoft Excel software in computer. The percentage of the liquefied residue content was calculated using the following Eq. (1):

$$\text{liquefied residue content (\%)} = \frac{\text{Mass of liquefied residue}}{\text{Mass of fermentation residue}} \times 100 \quad (1)$$

### 2.3. Separation and analysis procedure of the liquefied products and liquefied residues

The separation and analysis procedures of the liquefied products and liquefied residues are shown in Fig. 1. The liquefied products were mixed with deionized water at a 1:1 ratio. The precipitation occurs in the liquefaction product. The water-insoluble fraction and the water-soluble fraction were separated by centrifugation with a rotating speed of 4000 rpm. The water-soluble fraction was used for the follow-up the chloroform extraction. Because aluminum chloride was used as the catalyst in the liquefaction process, the water-soluble fraction necessarily contains aluminum metal ions and therefore cannot be directly determined by GC-MS. To remove the aluminum ions, sodium hydroxide was added in the water-soluble fraction, the precipitate was removed by centrifugation, and the liquid fraction residue was used for chloroform extraction.

At this time, the liquefied products were separated into three fractions: the water-insoluble fraction for FT-IR analysis, the chloroform extract fraction for GC-MS analysis, and the liquid fraction residue for IC analysis.

### 2.4. Isolation and purification of milled wood lignin (MWL)

**Isolation of raw MWL:** The fermentation residues were continuously fine ball-milled for 72 h. The milled samples were extracted (3 × 24 h) with dioxane/water 96:4 (v/v) (20 mL of solvent/g of milled samples). The solution was centrifuged, the supernatant was evaporated at 40 °C at a reduced pressure up to dryness, and the raw MWL was obtained.

**Purification of raw MWL:** The raw MWL was re-dissolved in a solution of acetic acid/water 9:1 (v/v) (15 mL of solvent/g of raw

**Table 1**  
Chemical composition (% dry weight) of reed and corn stover.

Chemical composition	Reed	Corn stover
Benzene-alcohol (2:1) extractive	8.39 ± 0.10	10.95 ± 0.07
Glucan	40.52 ± 0.03	38.75 ± 0.04
Xylan	25.86 ± 0.19	23.51 ± 0.18
Acid-insoluble lignin	16.22 ± 0.02	15.62 ± 0.16
Acid-soluble lignin	2.0 ± 0.1	2.4 ± 0
Ash	3.59 ± 0.14	3.65 ± 0.08

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