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# Acid−Chlorite Pretreatment and Liquefaction of Cornstalk in Hot-Compressed Water for Bio-oil Production

Hua-Min Liu,[†] Bing Feng,[‡] and Run-Cang Sun*[,†,§]

[†]State Key Laboratory of Pulp and Paper Engineering and [‡]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

[§]The Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, China

**ABSTRACT:** In this study, cornstalk was pretreated by an acid−chlorite delignification procedure to enhance the conversion of cornstalk to bio-oil in hot-compressed water liquefaction. The effects of the pretreatment conditions on the compositional and structural changes of the cornstalk and bio-oil yield were investigated. It was found that acid−chlorite pretreatment changed the main components and physical structures of cornstalk and effectively enhanced the bio-oil yield. Shorter residence time favored production of the total bio-oil products, whereas longer time led to cracking of the products. A high water loading was found to be favorable for high yields of total bio-oil and water-soluble oil. GC-MS analysis showed that the water-soluble oil and heavy oil were the complicated products of $C_{5-10}$ and $C_{8-11}$ organic compounds.

**KEYWORDS:** liquefaction, pretreatment, cornstalk

## INTRODUCTION

Energy shortages and environmental pollution are two crucial and serious problems we have to deal with.[1] Biomass has attracted more and more interest as an alternative energy source. Its use can contribute to the reduction of greenhouse-gas emissions because the $CO_2$ that is produced during the utilization of biomass can be reabsorbed by new growing biomass, thereby closing the $CO_2$ cycle.[2]

Liquefaction processes such as fast pyrolysis and solvolytic liquefaction of biomass have been studied recently. Fast pyrolysis, wherein biomass is subjected to rapid heating to high temperatures (400−1000 °C) under an inert atmosphere, was used to produce bio-oil on an industrial scale.[3] Solvolytic liquefaction of biomass has advantages over fast pyrolysis processes because it is conducted at much lower temperatures (<300 °C) in solvents (such as water, ethanol, and methanol) with and without the presence of catalysts.[4−6] Water (hot-compressed or sub/supercritical water) is an effective, cheap, and "green" solvent for the direct liquefaction of biomass. Although methods of converting biomass into transportation fuels are constantly improving and are advancing toward economical feasibility, the search for high-yielding biomass with low environmental impact is also ongoing.[7]

Plant biomass compositions, namely, cellulose, hemicelluloses, and lignin, are important parameters affecting product distributions. However, the lignin−carbohydrate complexes (LCC) and the crystalline structure of cellulose have limited accessibility to solvents during solvolytic liquefaction processes. Pretreatment that disrupts the LCC and the crystalline structure of biomass will help to overcome such obstacles. Presently, physical, chemical, or biological pretreatment methods (or their combination) are widely used to enhance liquefaction yields. Because the presence of lignin in biomass reduces accessibility to solvents in the process of liquefaction, it is helpful to remove some of the incorporated lignin and break down LCC to obtain better liquefaction yields. Removing lignin from biomass can be achieved by various methods. Alkaline peroxide processes are effective for both delignification and removal of hemicelluloses, but their use is limited due to extensive degradation of cellulose by the peroxide radical.[8] However, acid−chlorite delignification utilizing an aqueous solution of acetic acid and sodium chlorite is perhaps the most popular and well-established method for degrading residual lignin in pulps at moderate temperatures in bleaching processes.[9]

Many researchers have studied pretreatment methods to increase the accessible surface area of lignocellulose and improve biomass digestibility at the enzymatic hydrolysis stage, which is the key to biomass conversion.[10−12] However, as far as we know, few attempts have been made to use pretreatment methods for enhancing bio-oil yield. The objective of this investigation was to develop an improved and effective pretreatment process by using acid−chlorite as active reagent aimed to reduce the energy input and enhance bio-oil yields for solvolytic liquefaction of cornstalk. Thus, cornstalk biomass was pretreated with acid−chlorite to partially remove lignin and hemicelloloses and then was liquefied by hot-compressed water in a stainless steel reactor (0.5 L). The effects of temperature, residence time, and solvent loading on the liquefaction of biomass before and after pretreatment in hot-compressed water were comparatively studied.

## MATERIALS AND METHODS

**Material.** The cornstalk sample was collected from the city of Guangzhou, which is located in southern China. The raw material was first ground using a high-speed rotary cutting mill and sieved through 40 mesh. The ground cornstalk was extracted with distilled water and ethanol, then dried at 105 °C for 24 h, and kept in desiccators at room temperature. The ash of cornstalk was determined by burning at 650 °C.

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Ultimate analysis of the sample was carried out on a CHNO Elemental Analyzer Vario EL (Elementar, Germany). The composition of oxygen (O) was estimated by difference. The higher heating value (HHV) of the sample was calculated on the basis of Dulong's formula

$$\mathrm{HHV\ (MJ/kg)} = 0.3383C + 1.442(H - O/8) \quad (1)$$

in which $C$, $H$, and $O$ represent the weight percentages of carbon, hydrogen, and oxygen, respectively.

Analysis showed that the cornstalk used in this study contained about 5.5% ash, 45.33% carbon, 47.69% oxygen, 6.07% hydrogen, and 0.91% nitrogen (on a dry basis). The sample had a HHV of 16.4 MJ/kg.

**Pretreatment.** Acid−chlorite treatment of cornstalk sample was performed in a reciprocating water bath using sodium chlorite and acetic acid at 75 °C. Each sample was placed in a triangle flask (2 L) with deionized water (6 mL/g biomass), sodium chlorite (0.2 mg/g biomass), and glacial acetic acid (0.2 mL/g biomass). Each triangle flask was then sealed and placed in a water bath at 75 °C. Every dose of sodium chlorite and glacial acetic acid was added, and the flask was resealed and placed back in the water bath at 75 °C after each 0.5 h. After totals of 1, 1.5, and 3 h, respectively, the samples were removed from the bath, and the solids were filtered through a sintered glass filter, washed with copious amounts of deionized water until the filtrate pH was neutral, and then dried at 105 °C for 24 h and kept in desiccators at room temperature before use.

**Experimental Procedure.** Liquefaction experiments were carried out in a 0.5 L Greatest Common Factor (GCF) type autoclave. It was rated up to a working pressure of 20 MPa and a working temperature of 350 °C. A heavy-duty magnetic drive stirrer was installed for mixing. A type-J thermocouple was fitted into the reactor for direct temperature measurement of the reaction media. A standard pressure gauge was installed on the reactor head. A Proportional-Integral-Derivative (PID) controller was used to control the temperature of the reactor.

For each run, cornstalk and water were fed into the 0.5 L magnetically driven stirred autoclave. Then the reactor was purged three times with nitrogen to remove the air/oxygen in the reactor airspace. Agitation was set at 300 rpm and maintained for all experiments. The reactor was heated, and the temperature was maintained at the set temperature for the desired holding time. Afterward, it was cooled to room temperature by cool water.

The procedure of separating liquefaction products is shown in Figure 1. Once the reactor was cooled to room temperature, the gas product was vented without being further analyzed. The autoclave contents were poured into a beaker. The liquefied products were removed from the autoclave by washing with 150 mL of deionized water three times, and then they were filtered. After removal of the mixture under reduced pressure at 85 °C in a rotary evaporator, the aqueous phase product was designated water-soluble oil (WSO). The solid products were extracted with acetone (150 mL) in an extraction apparatus until the solvent in the thimble became colorless. After removal of the acetone under reduced pressure in a rotary evaporator, this fraction was weighed and designated heavy oil (HO). The acetone-insoluble fraction was dried at 105 °C and then weighed, and designated the solid residue.

**Analysis.** Bio-oil (WSO and HO) was determined with a gas chromatograph−mass spectrometer (GC-MS). GC-MS analyses were conducted on a model 7890A/5975 Trace GC/Palaris Q GC-MS spectrometer (Agilent, USA) using a carbon capillary column (HP-5MS, 30 m × 0.25 $\mu$m × 0.25 $\mu$m), with He as the carrier gas. The column temperature of the GC used in this study was programmed from 40 to 300 °C at a rate of 5 °C/min. The temperature of the injection chamber was 300 °C, and the injection size was 1 $\mu$L. Mass range was $m/z$ 30−500. The compounds were identified by a comparison with the NIST Mass Spectral Database.

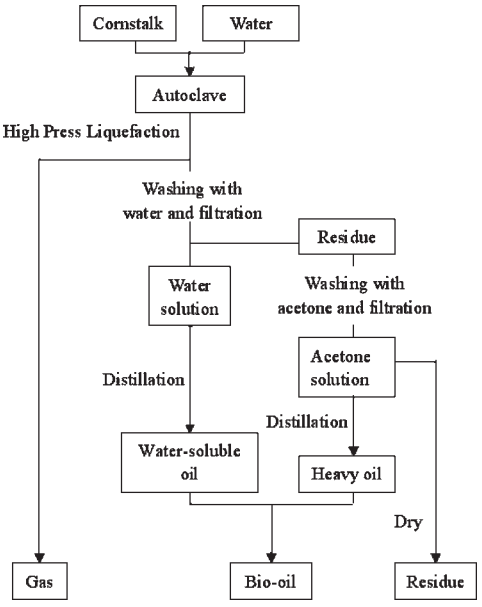


**Figure 1.** Procedure for separation of products.

The chemical components of raw and pretreated cornstalk were determined, in which the cellulose was determined by $HNO_3$/ethanol method.[13] For the determination of lignin and hemicelluloses, holocellulose was determined according to Chinese standard methods.[13] The contents of lignin and hemicelluloses were calculated as biomass − holocellulose − insoluble ash and holocellulose − cellulose, respectively.

A model S-3700N field emission scanning electron microscope (Hitachi, Japan) was used to image the dried fiber fraction of unpretreated and pretreated cornstalks. The ash content of the cornstalk was determined by burning at 650 °C.

## RESULTS AND DISCUSSION

**Effects of Acid−Chlorite Pretreatment on the Composition and Structure of Cornstalk.** *Changes in Composition of Cornstalk after Pretreatment.* Many researchers have proposed various biomass conversion mechanisms in hot-compressed water systems. Hemicelluloses would be the first to decompose at a low temperature (180 °C) followed by intermediate temperature lignin decomposition, whereas cellulose decomposes at relatively higher temperatures (>230 °C).[14] Due to different bio-oil formation temperatures for cellulose, hemicelluloses, and lignin, the optimum temperature for bio-oil yield may depend on the relative abundance of cellulose, hemicelluloses, and lignin in a biomass feedstock. Therefore, the composition of biomass is a key factor affecting the efficiency of bio-oil production during conversion processes.

The acid−chlorite delignification pretreatment is considered to be greatly affected by the composition of the biomass, whereas the composition could be changed during the acid−chlorite pretreatment process due to the complex physical and chemical roles of acid−chlorite. In this study, the unpretreated and pretreated cornstalks were analyzed to investigate the changes of main composition after pretreatment. The analysis results are shown in Figure 2. Clearly, the unpretreated and pretreated cornstalks differ in cellulose, hemicellulose, and lignin contents. For unpretreated materials, the contents of cellulose, hemicellulose, and lignin were 45.2, 28.2, and 21.1%, respectively. The contents of cellulose were enhanced by the pretreatment as

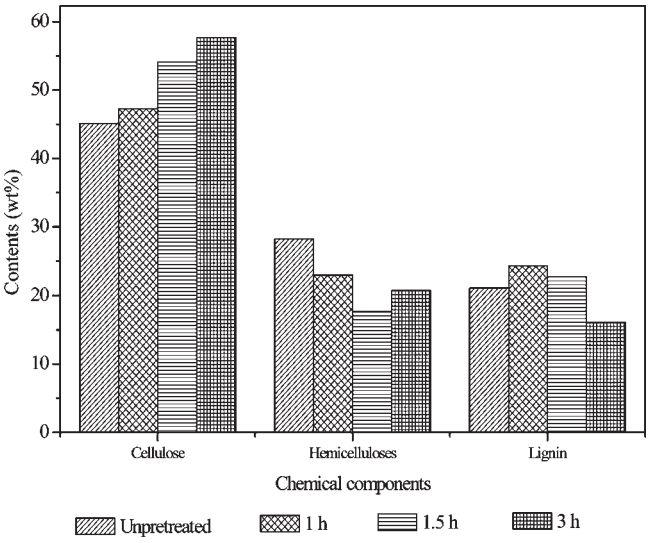


**Figure 2.** Chemical composition of the unpretreated and pretreated cornstalks.

compared to unpretreated cornstalk and increased with the increment of pretreatment time. After the shorter time pretreatment, the content of hemicelluloses decreased to 22.9% (1 h) and 17.7% (1.5 h), whereas the content of lignin increased to 24.2% (1 h) and 22.7% (1.5 h). The results indicated that the shorter time pretreatment partly removed hemicelluloses but did not markedly remove the lignin. Acid−chlorite acted on lignin in biomass, but it could also affect the polysaccharides. The possible reason was that the addition of acid increased the likelihood of chain degradation of hemicelluloses due to acid hydrolysis. However, the lignin content of the cornstalk pretreated for 3 h was 16.1%, which was lower than the content of 21.1% for unpretreated cornstalk. This indicated that the lignin content of the cornstalk was significantly reduced after the pretreatment for a longer time, and hemicellulose removal by disruption of lignin−carbohydrate complex (lignin−hemicelluloses) linkages may have resulted in the decrease of lignin content.

*Scanning Electron Microscope (SEM) Observations of Cornstalk Structure.* Acid−chlorite has been recognized as one of the most effective agents for swelling of biomass. It primarily acts on lignin in biomass, but it can also affect the polysaccharides. A SEM was used to compare physical cornstalk structure changes during the delignification pretreatment with acid−chlorite. The microstructures of unpretreated and pretreated cornstalks by acid−chlorite are shown in Figure 3. The surface of unpretreated cornstalk was integrated and smooth, whereas the cornstalks pretreated with acid−chlorite had a destroyed structure, because lignin was greatly destroyed by acid−chlorite and generated many grooves. By further observation, there was much anomalous porosity, with a gross estimate of 1−2 $\mu$m in diameter, in the pretreated fibril. However, cell wall structure was not disrupted by the pretreatment. Koo et al.[15] studied the organosolv pretreatment of biomass showed that lignin was isolated and migrated onto surface of biomass during the delignification process and the isolated and migrated lignin from lignin droplets on the surface. However, in our experiment, the SEM images did not show any lignin droplets on the surface due to lignin dissolution by acid−chlorite. As a result, the observations indicated that the acid−chlorite delignification process disrupted the physical

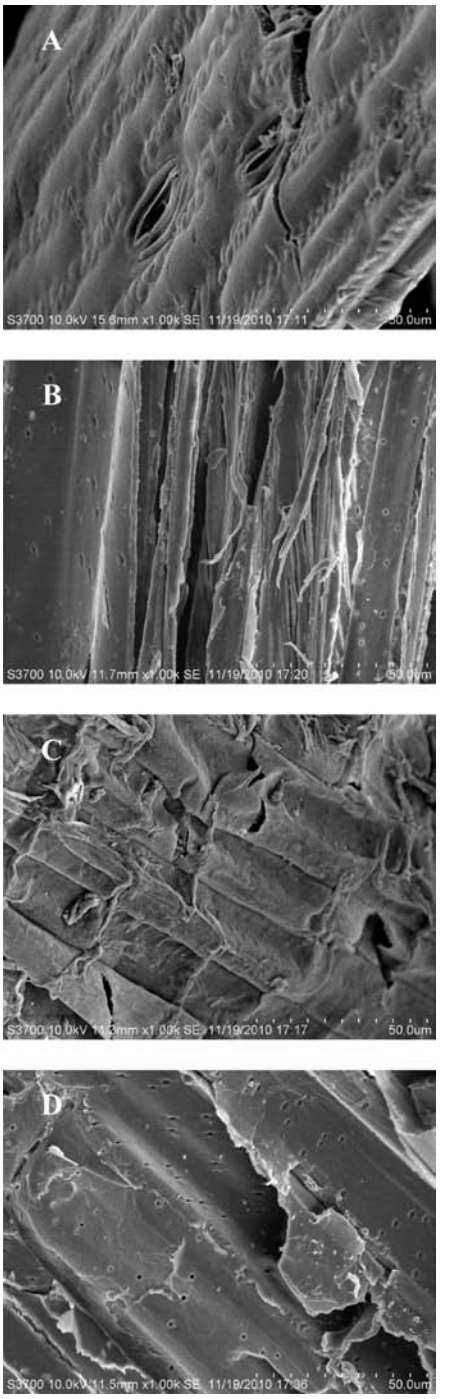


**Figure 3.** SEM images of the unpretreated and pretreated cornstalks: (A) unpretreated cornstalk; (B) cornstalk pretreated for 1 h; (C) cornstalk pretreated for 1.5 h; (D) cornstalk pretreated for 3 h.

structural barrier of cornstalk and led to the fine fibrils having more surface area and roughness.

**Liquefaction of the Unpretreated and Pretreated Cornstalks in Hot-Compressed Water.** As an effective pretreatment method, acid−chlorite delignification was first used to deal with cornstalk to break down LCC and separate carbohydrates and lignin for the liquefaction process. In this study, acid−chlorite delignification was introduced to pretreat the cornstalk to investigate the effect on liquefaction. The effects of reaction temperature,

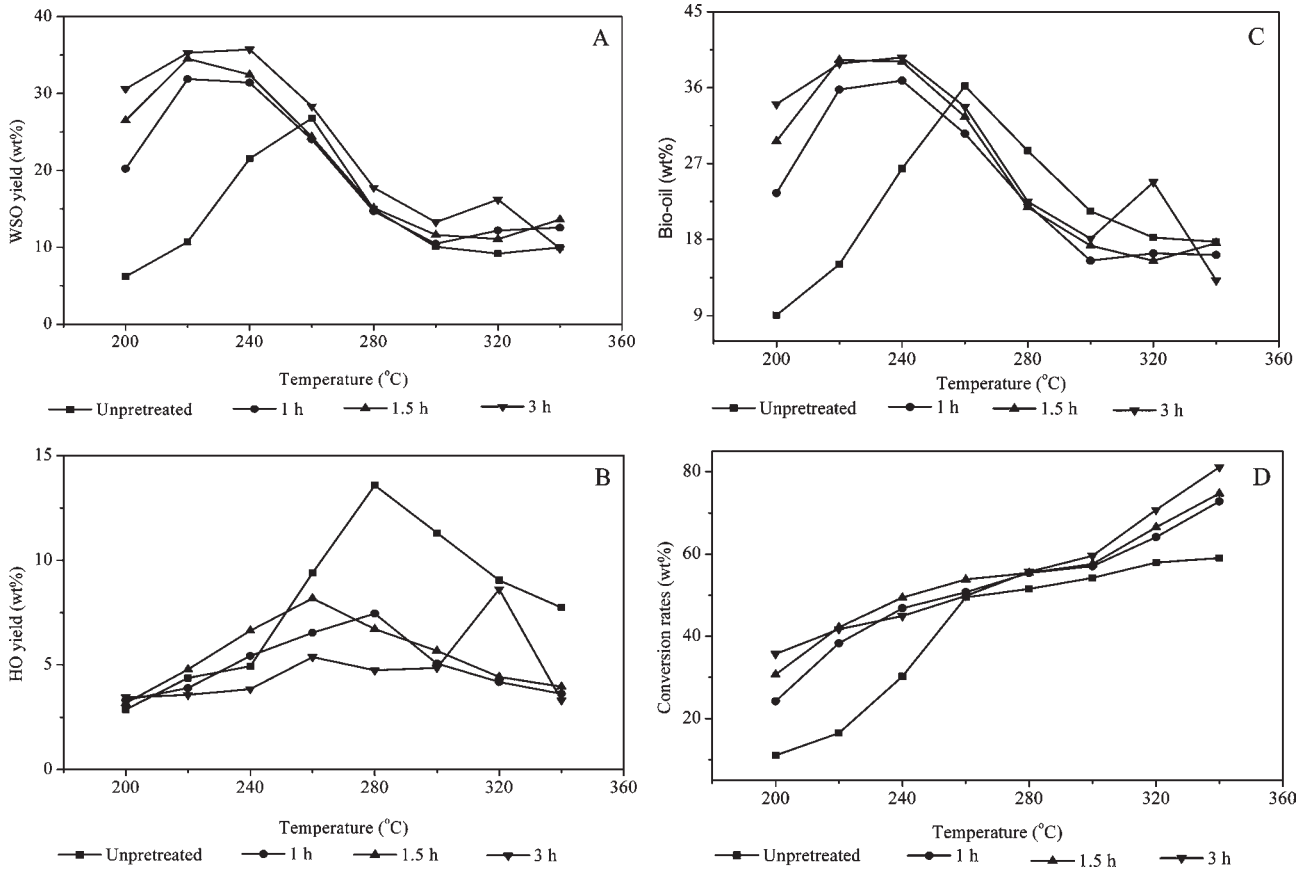


**Figure 4.** Effect of reaction temperature on product yields in the liquefaction of the unpretreated and pretreated cornstalks: (A) WSO yield at different temperatures; (B) HO yield at different temperatures; (C) bio-oil yield at different temperatures; (D) conversion rates at different temperatures.

residence time, and water amount were studied in the hot-compressed liquefaction of the unpretreated and pretreated cornstalk process.

*Effect of Temperature.* One of the most important parameters accelerating the reaction rate in the hydrothermal liquefaction process is the temperature. The effect of temperature on unpretreated and pretreated cornstalk conversion is shown in Figure 4. These experiments were conducted under standard conditions of 5 g of cornstalk (unpretreated or pretreated) in 50 mL of water with 0 min residence time. It can be seen from Figure 4D that the conversion of these cornstalks increased with rising temperature. The reactor temperature influences the pressure and whether the water was in the liquid state, the gaseous state, or sub- and supercritical states. In general, the lower the temperature and pressure, the higher the char yield. This correlates with low temperature and pressure favoring hydrothermal carbonization and high temperature and pressure favoring hydrothermal liquefaction.[16] The total conversion rate (100% − residue yield) from liquefaction of the pretreated cornstalks was much higher as compared to the total conversion rate from the liquefaction of unpretreated cornstalk. This was due to the changes of the structure and chemical components, which made it easy for the liquefaction reagent to enter into the cornstalk.

The liquid products, which are the targeted products in cornstalk liquefaction, were composed of WSO and HO.[17] WSO primarily formed from the conversion of cellulose and hemicelluloses via depolymerization and hydrolysis reactions. In contrast, the HO results from the pyrolysis/hydrolysis/degradation of lignin or from the dehydration of intermediate products derived from holocellulose.[18,19] As shown in Figure 4A−C, the influence of temperature on the yield of bio-oil products seems sequential: initially, the rise in temperature triggers bio-oil yield; after maximum bio-oil yield has been reached, further increase in temperature actually inhibits cornstalk liquefaction. It is worth noting that increasing the temperature to 320 or 340 °C resulted in a slight increase in WSO yields from liquefaction of these samples. The possible reason may be that water served as both reaction medium and reactant, and hot-compressed water at higher temperature was more suitable for free radical reactions.[20] The conversion of free radicals to oil fraction was promoted in the presence of water, resulting in the increment of oil yield at higher temperatures. The maximum bio-oil, WSO, and HO yields from liquefaction of unpretreated cornstalk were 36.3% (260 °C), 26.8% (260 °C), and 13.8% (280 °C), respectively. Comparatively, the pretreated cornstalk conversions showed higher bio-oil and WSO yields, but lower HO yield as compared to that of unpretreated cornstalk liquefaction. For example, the maximum bio-oil, WSO, and HO yields from liquefaction of the pretreated cornstalks were 39.6% (240 °C), 35.7% (240 °C), and 8.2% (260 °C), respectively. It can be concluded that the pretreatment markedly enhanced the bio-oil and WSO yields but decreased the HO yield and optimum temperature as compared to the untreated sample. There were two reasons for this. One was the changes of the physical characteristics resulting in the increase in specific surface area and porosity. The second reason was that the complex structure of lignin and hemicelluloses with

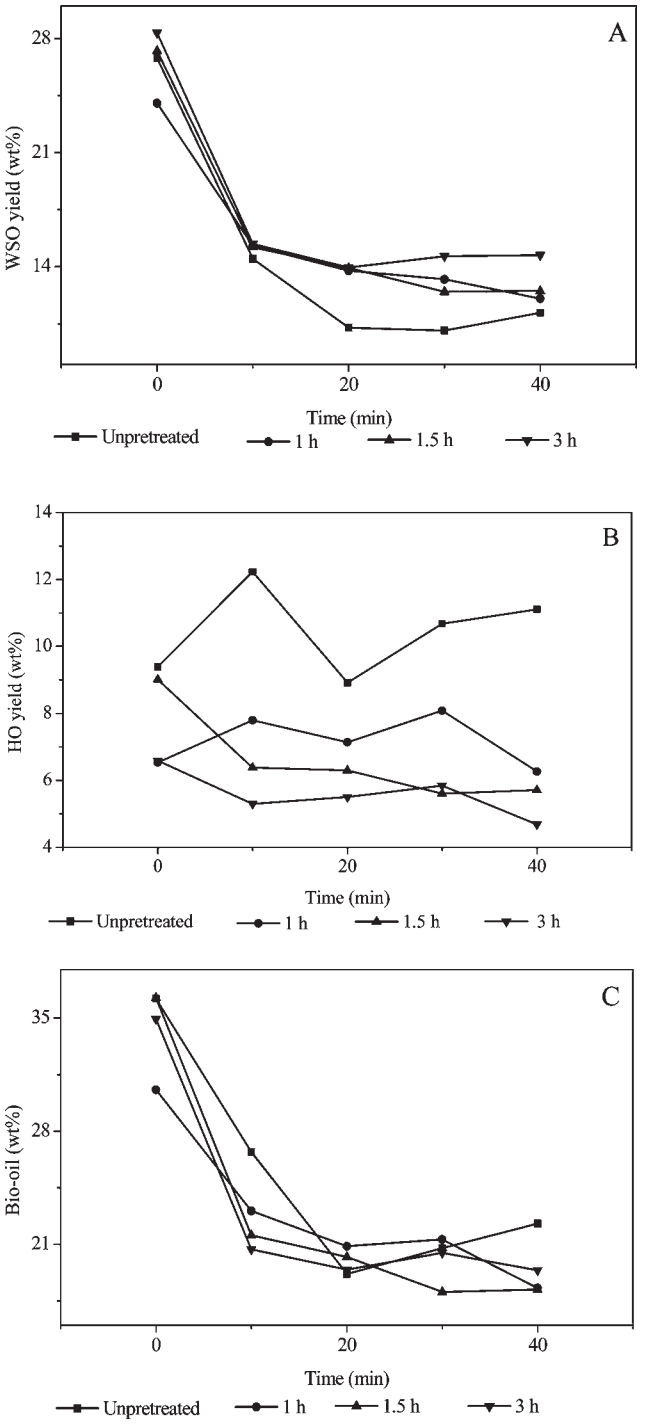


**Figure 5.** Effect of residence time on bio-oil yield in the liquefaction of the unpretreated and pretreated cornstalks: (A) WSO yield at different times; (B) HO yield at different times; (C) bio-oil yield at different times.

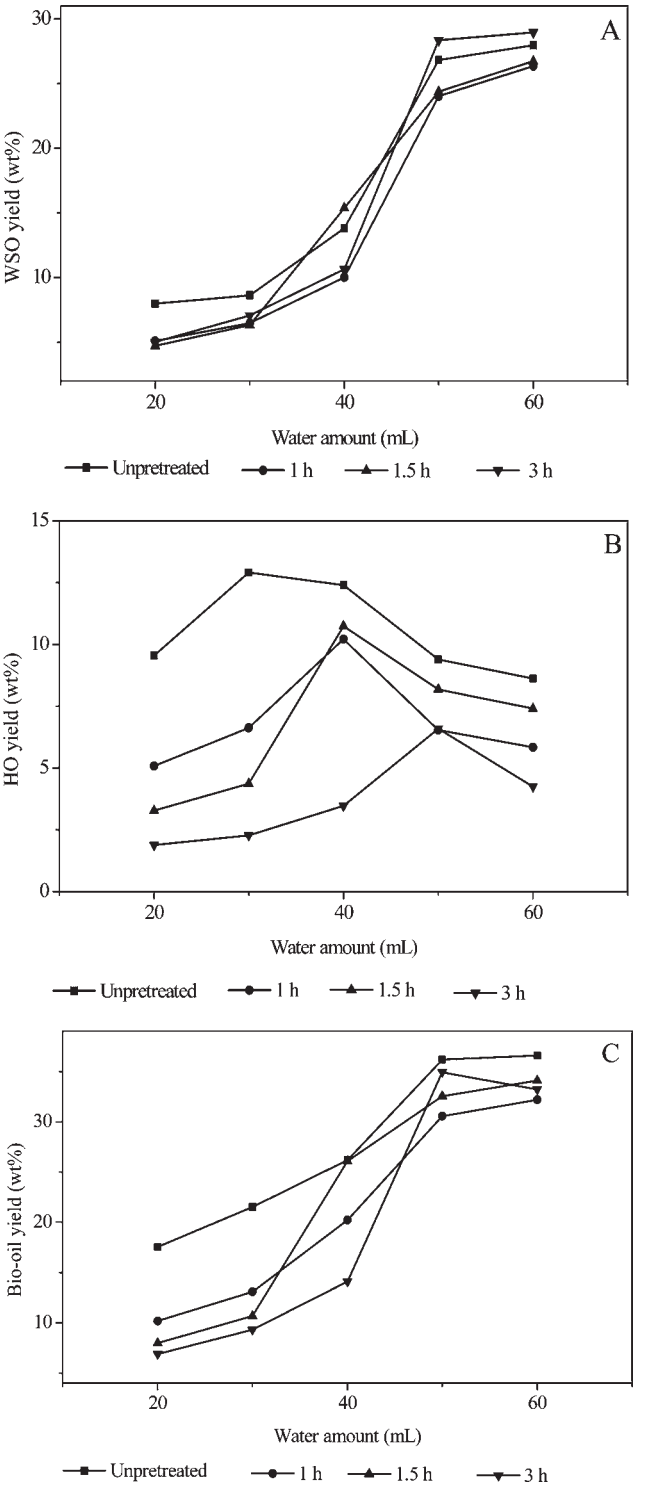


**Figure 6.** Effect of water amount on bio-oil yield in the liquefaction of the unpretreated and pretreated cornstalks: (A) WSO yield at different water amounts; (B) HO yield at different water amounts; (C) bio-oil yield at different water amounts.

cellulose was destroyed after acid−chlorite pretreatment, resulting in the remaining cellulose and hemicelluloses being more accessible to degradation and improving the WSO and total bio-oil yields.

*Effect of Residence Time.* There may be many reasons to the effect of residence time in liquefaction. In hydrothermal medium, there are always chances for the secondary and tertiary reactions. These reactions can convert heavy intermediates into liquids, gases, or residue species.[21] Figure 5 shows the effect of residence time on bio-oil yield in the hydrothermal liquefaction of unpretreated and pretreated cornstalks. With an operating temperature of 260 °C and 5 g of sample in 50 mL of water, the WSO yields obtained from liquefaction of these samples decreased about

**Table 1. GC-MS Analysis Results for the WSOs Obtained from Liquefaction of the Four Samples at 300 °C**

| | | content (%) | | | | | |
|---|---|---|---|---|---|---|---|
| RT (min) | compound | untreated | 1 h | 1.5 h | 3 h | formula | $M_w$ |
| 15.12 | 1,2-cyclopentanedione, 3-methyl- | | | 3.9 | | $C_6H_8O_2$ | 112 |
| 15.16 | 2-cyclopenten-1-one, 2-hydroxy-3-methyl- | 3.6 | 4.4 | | 2.7 | $C_6H_8O_2$ | 112 |
| 20.19 | pentanoic acid, 4-oxo- | | 4.7 | 3.7 | 5.4 | $C_5H_8O_3$ | 116 |
| 21.42 | pentanoic acid, 2-methyl-4-oxo- | | 1.2 | | | $C_6H_{10}O_3$ | 130 |
| 21.53 | acetic acid, pentyl ester | | | 1.2 | | $C_7H_{14}O_2$ | 130 |
| 24.67 | 1,2-benzenediol | 6.2 | 11 | 6.6 | 4.4 | $C_6H_6O$ | 110 |
| 25.96 | 1,2-benzendiol, 3-methoxy- | | | | 2.2 | $C_7H_8O_3$ | 140 |
| 27.89 | 2-cyclopenten-1-one, 6-methyl-3-(1-methylethyl)- | 3.9 | | | | $C_{10}H_{16}O$ | 152 |
| 27.98 | resorcinol | | | | 2.5 | $C_6H_6O_2$ | 110 |
| 28.18 | 2-cyclopenten-1-one, 2,3-dimethyl- | | | 1.2 | | $C_7H_{10}O$ | 110 |
| 28.46 | 2-cyclohexen-1-one, 6-methyl-3-(1-methylethyl)- | | 6.9 | | | $C_{10}H_{16}O$ | 152 |
| 28.51 | phenol, 2,6-dimethoxy- | 7.2 | 10 | 4.1 | 2.5 | $C_8H_{10}O_3$ | 154 |
| 30.53 | furan, 2-ethyl-5-methyl- | | 3.2 | | | $C_7H_{10}O$ | 110 |
| 32.37 | ethanone, 1-(2-hydroxy-4-methoxyphenyl)- | 4.9 | | | | $C_9H_{10}O_3$ | 166 |
| 33.5 | 2-propanone, 1-(4-hydroxy-3-methoxyphenyl)- | 1.3 | 1.7 | 2.7 | | $C_{10}H_{12}O_3$ | 180 |
| 36.25 | 1,2,4-benzenetriol | | | | 6.5 | $C_6H_6O_3$ | 126 |
| 38.06 | ethanone, 1-(4-hydroxy-3,5-methoxyphenyl)- | 3.8 | | | | $C_{10}H_{12}O_4$ | 196 |
| 45.13 | 9,12-octadecadienoic acid (2,2)-, methyl ester | 1.7 | | | 1.4 | $C_{19}H_{34}O_2$ | 294 |
| 45.26 | 9-octadecenoic acid (2)-, methyl ester | 2.4 | | 2.9 | | $C_{19}H_{36}O_2$ | 296 |
| 48.65 | octadecane | 1.4 | | | | $C_{18}H_{28}$ | 254 |

twice more with increased residence time from 0 to 40 min, and it was found that a 0 min residence time at this condition was sufficient for the cornstalks to form oily compounds by giving the highest total bio-oil yield. Increasing the residence time resulted in a decrease of the bio-oil yield, indicating polymerization of the newly formed compounds. Most researchers agree that bio-oil yield is higher with shorter residence times, as prolonged reactions can decompose and or condense bio-oil to low molecular chemicals and solid char/tar.[22] Therefore, operating a reactor system of a shorter residence time is favorable because the rate of production will be higher and heat loss per unit mass of bio-oil produced could be significantly lower for an immovable reactor volume, making the process more energy efficient.

As shown in Figure 5B, it is clear that the time markedly influences the HO yields obtained from liquefaction of unpretreated cornstalk and pretreated cornstalk (at the time of 1 h). This was caused by the competition between the two reactions (hydrolysis and repolymerization) involved in the liquefaction.[23] Comparatively, the HO yields obtained from liquefaction of pretreated cornstalks (at times of 1.5 and 3 h) decrease with increasing residence time. The distinctive structural characteristics of biomass make it resistant to attack by solvent during the liquefaction process.[24] Therefore, the different trends of HO yields from liquefaction of these samples were that the longer pretreatment broke down the complex structure and changed the reaction pathways of liquefaction.

*Effect of Water Amount.* The effect of water amount on the bio-oil yields obtained from liquefaction of these four samples is depicted in Figure 6. These experiments were carried out at 260 °C, 5 g of cornstalk sample, and 0 min resistance time. Clearly, the larger water amount had positive effects on the bio-oil and WSO yields. Bio-oil and WSO yields obtained from liquefaction of all these samples increased with the water amount increasing from 20 to 50 mL. Similarly, Akhtar et al.[25] also found that larger water amounts resulted in higher bio-oil yield. This may be because small amounts of water were unable to dissolve cornstalk samples possibly due to the decrease in dissolving power of solvent compared to amount of substrate, which may result in low dissolutions. More water would be preferred for liquefaction conversation. However, less cornstalk in water requires more energy to heat the water to certain temperatures. From an economic perspective, it would be uneconomical to use a large amount of water that may require higher energy inputs and wastewater treatment. However, it is worth noting that the bio-oil yield obtained from liquefaction of the cornstalk at the pretreatment time of 3 h slightly decreased when the water amount was further increased to 60 mL. This result suggested that the pretreatment and the water amount had a synergetic effect on the bio-oil yield as compared to the liquefaction of unpretreated cornstalk experiment. The yield of HO increased with the water amount increasing first and decreased with the water amount increasing in liquefaction of all four sample processes. This might be due to the competition between the two reactions (hydrolysis and repolymerization) involved in the liquefaction.

**GC-MS Analysis of the Bio-oils.** Liquefaction bio-oils not only are used as fuel in diesel engines and boilers but also constitute valuable organic chemicals.[24] Properties of bio-oil products were another interest of this work in addition to the liquefaction yields. Thus, GC-MS was used to identify the chemical composition of the WSO and HO produced by liquefaction of the unpretreated and pretreated cornstalks, where the liquefaction operations were carried out at 260 °C for 0 min in 50 mL of water. The area percentages of each compound (defined by the percentage area for each peak in the chromatogram in relation to the total area) are shown in Tables 1 and 2, listing the major compounds detected by GC-MS. The area percent may be used to show the relative concentrations of the compound in the WSO and HO.

Table 2. GC-MS Analysis Results for the HOs Obtained from Liquefaction of the Four Samples at 300 °C

| RT (min) | compound | content (%) | | | | formula | $M_w$ |
|---|---|---|---|---|---|---|---|
| | | untreated | 1 h | 1.5 h | 3 h | | |
| 6.2 | *p*-xylene | 1.3 | 1.4 | | 1.3 | $C_8H_{10}$ | 106 |
| 6.3 | *N*-benzylglycine ethyl ester | | | 7.3 | | $C_{11}H_{15}NO_2$ | 193 |
| 6.8 | benzene, (1-methylethyl)- | 1.2 | 0.9 | 1.3 | 1.2 | $C_9H_{12}$ | 120 |
| 7.3 | benzene, propyl- | 5.9 | 5.4 | | 6.1 | $C_9H_{12}$ | 120 |
| 7.4 | benzene, 1-ethyl-4-methyl- | | | 20.3 | | $C_9H_{12}$ | 120 |
| 7.5 | benzene, 1-ethyl-2-methyl- | 22.8 | 19.5 | | 21.5 | $C_9H_{12}$ | 120 |
| 7.6 | benzene, 1,3,5-trimethyl- | 2.7 | 2.6 | 3.2 | 9.9 | $C_9H_{12}$ | 120 |
| 7.9 | *cis*-1*H*-indene, octahydro- | 0.6 | | | | $C_9H_{16}$ | 124 |
| 8.0 | benzene, 1,2,3-trimethyl- | 8.9 | 12.8 | 11.6 | 1.9 | $C_9H_{12}$ | 120 |
| 8.1 | decane | 0.9 | | 1.2 | 1.1 | $C_{10}H_{22}$ | 142 |
| 8.4 | 1,3-dimethyl-1-cyclohexene | | | | 0.19 | $C_8H_{14}$ | 110 |
| 8.8 | indane | 11.2 | 10.2 | 13.4 | 9.1 | $C_9H_{10}$ | 118 |
| 9.1 | naphthalene,1,2,3,5,8,8a-hexahydro- | | | 0.23 | | $C_{10}H_{14}$ | 134 |
| 9.2 | 4,7-methano-1*H*-indene, octahydro- | | | 0.48 | | $C_{10}H_{16}$ | 136 |
| 11.4 | *N*-methyl-1-octadecanamine | 0.33 | | | | $C_{19}H_{51}N$ | 283 |
| 12.8 | *N*-(2-furfuryl)thiophene-2-carboxamide | | 1.7 | | | $C_{10}H_9O_2NS$ | 207 |

As a result of the disintegration of the cellulose, hemicelluloses, and lignin, the liquefaction bio-oils might be transformed into products having different molecular structures.[26] For example, the phenolic compounds primarily originated from degradation of lignin and they might also form from cellulose via hydrolysis to sugars followed by dehydration and ring closure reactions;[27] as widely agreed by many researchers,[18,19] the furan derivatives and the acid were formed primarily from the conversion of cellulose and hemicelluloses via depolymerization and hydrolysis reactions. It can be seen that the compositional differences were relatively large among the WSO and HO originating from various samples. The differences of structure and components between unpretreated and pretreated cornstalks can contribute to that distinction. It can be concluded that the pretreatment had an important effect on the formation of various compounds in the liquid products. Results indicated that the WSO and HO from hydrothermal liquefaction of these samples comprised very complex mixtures of organic compounds of 5−10 and 8−11 carbons, respectively. The various compounds found in the WSO products can be classified as hydrocarbons (alkanes, alkenes), phenols and alkylated derivatives, aromatics with a single ring (benzene, toluene), carboxylic acids, carbonyls, and furans. Phenol and phenolic compounds (e.g., *p*-xylene, 1-methylethylbenzene, propylbenzene, 1-ethyl-4-methylbenzene, 1-ethyl-2-methylbenzene, 1,3,5-trimethylbenzene, and 1,2,3-trimethylbenzene) were the major components of all four types of HOs. In addition, there were also a variety of alkanes (e.g., decane), cycloalkane and cycloalkene derivatives (e.g., 1,2,3,5,8,8a-hexahydronaphthalene), and furan derivatives (e.g., *n*-(2-furfuryl)thiophene-2-carboxamide). Because of the complexity in bio-oil compositions, it was very difficult to identify the reaction pathways of these compounds.

## AUTHOR INFORMATION

### Corresponding Author

*Postal address: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China. Phone: +86-20-87111861. Fax: +86-20-8711186. E-mail: rcsun@scut.edu.cn.

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