Conversion of Cornstalk to Bio-oil in Hot-Compressed Water: Effects of Ultrasonic Pretreatment on the Yield and Chemical Composition of Bio-oil, Carbon Balance, and Energy Recovery

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Ⓢ *Supporting Information*

ABSTRACT: An ultrasonic pretreatment method was developed to enhance the yield of bio-oil obtained from the liquefaction of cornstalks in hot-compressed water at different reaction temperatures (260−340 °C) and residence times (0−40 min). Influences of ultrasonic pretreatment on the physicochemical properties of cornstalks and bio-oil yields were investigated. The results show that ultrasonic pretreatment obviously increases surface areas of cornstalks, decreases crystallinities, and erodes the structures of lignin, leading to more exposure of cellulose and hemicellulose. The yield of bio-oil was increased remarkably by 10.1% for 40 min sonicated cornstalks under the optimum liquefied conditions (300 °C for 0 min of residence time). Carbon balance indicates that ultrasonic pretreatment increases the carbon conversion of cornstalks to heavy oil and water-soluble oil. Energy balance indicates that the sonicated cornstalks have positive energy efficiencies. GC-MS analyses demonstrate ultrasonic pretreatment increases the contents of the phenols in heavy oil and water-soluble oil.

KEYWORDS: *ultrasonic pretreatment, cornstalk, liquefaction, bio-oil, hot-compressed water*

■ INTRODUCTION

The growing demand for fossil fuels and concern about global climate change have allowed people to focus considerable attention on green and renewable biofuels, which are becoming a viable alternative to fossil fuels.[1,2] Agricultural wastes such as cornstalks, wheat straw, and rice straw have huge potentials for preparing bio-oil due to the advantages of large-scale production, low cost, and no "food versus fuel" conflict.[3] Meanwhile, the conversion of agricultural wastes to bio-oil helps reduce air pollution from direct combustion in the fields.

The thermal−chemical conversion approaches are considered to be simple, effective, and provided with promising industrial scale-ups for the conversion of biomass to bio-oil, which mainly involves two typical processes: pyrolysis and liquefaction.[4,5] Pyrolysis is normally performed at the high-temperature condition (500−800 °C) and has severe requirements for the particle size (≤0.2 mm) and the moisture content of biomass (≤10%),[6] whereas liquefaction can be carried out at relatively low temperatures (250−350 °C) using flexible and various biomasses.[7] Especially when water is selected as reaction medium and solvent, the drying process of biomass is exempted. Hydrothermal liquefaction can directly deal with the wet biomass with high efficiency as in pyrolysis. Therefore, hydrothermal liquefaction has lower energy consumption and easier process integration, which is drawing more and more attention.

The liquefaction of biomass in hot-compressed water has been investigated extensively in recent decades. Various biomasses involving agricultural wastes, woody materials, algae, and animal manures have been successfully converted into bio-oils by hydrothermal liquefaction.[8,9] However, the commercial application of hydrothermal liquefaction still suffers from many challenges due to high investment costs and existing technical obstacles.[8] One of the major challenges is the low yield of bio-oil and conversion of biomass feedstock. There are three main reasons: (1) The complex and rigid structures of biomass composed of lignin, cellulose, and hemicellulose result in high resistance to chemical degradation.[10] Lignin is more obstinate and difficult to degrade in hot-compressed water. The natural integument formed by lignin hinders the degradation of cellulose and hemicellulose and reduces the bio-oil yield. (2) The nature of strong interactions among lignin, cellulose, and hemicellulose leads to low accessible surface area of biomass, which causes a decrease of the decomposition rate in hot-compressed water.[11] However, long reaction time will lead to the secondary and tertiary decompositions of bio-oil and decrease the bio-oil yield. (3) The high crystallinity of cellulose also limits its accessibility to solvents. Effectively solving these problems becomes urgent and essential to the large-scale application of hydrothermal liquefaction. Using acid or alkali catalysts in the process of liquefaction is the most common way to increase the bio-oil yield.[12,13] However, the acid or alkali catalysts are difficult to recycle and dispose of. Thus, it is necessary to develop a novel approach to improve the bio-oil yield.

Ultrasonic pretreatment is a physical and green method and has efficacies of eroding the structure of biomass, increasing the surface area and accessibility, and generating activate biomass.[14,15] Extensive research related to the utilization of ultrasonic pretreatment has been reported in the bioethanol preparation field.[16−18] The results indicate that ultrasonic
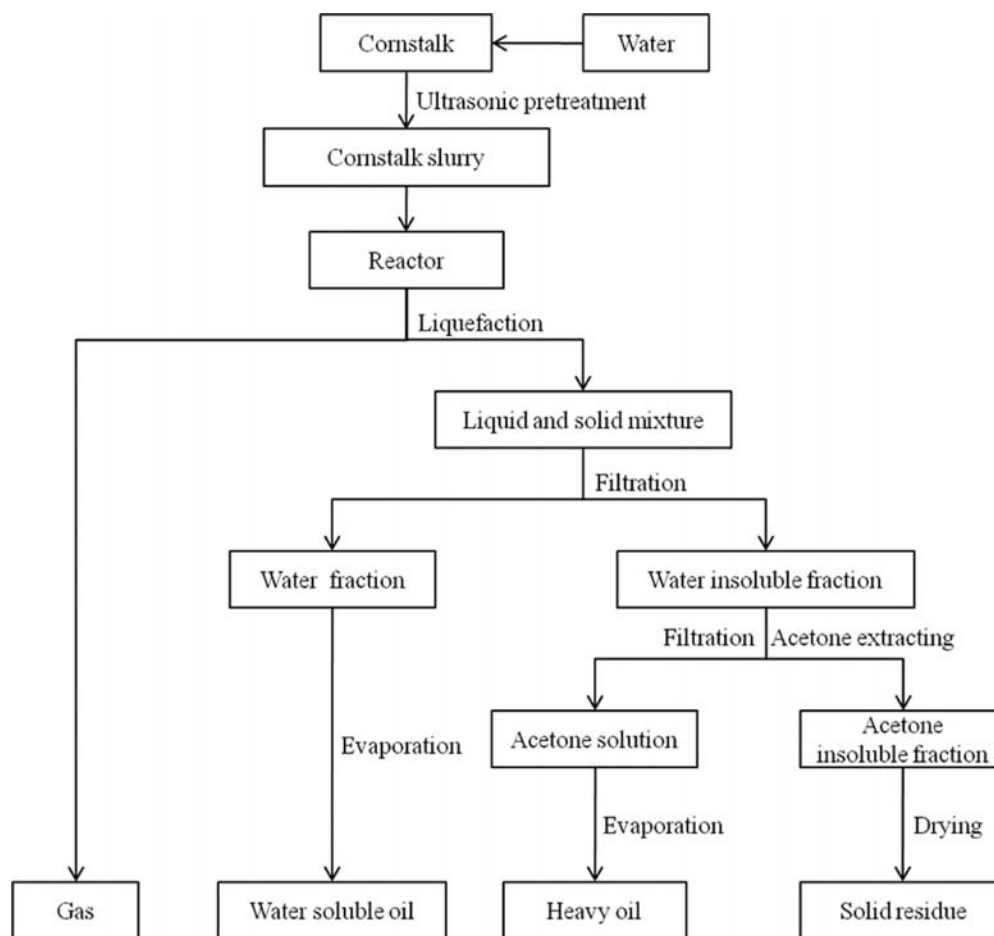
Figure 1. Separation and preparation procedures of products liquefied from cornstalks in hot-compressed water.

pretreatment significantly enhances the yield of bioethanol. We also first declared the study on the conversion of cellulose (one of the main components in biomass) to bio-oil in hot-compressed water with ultrasonic pretreatment.[19] The results show that ultrasonic pretreatment results in an excellent swelling and dispersion of cellulose in the water. The bio-oil yield was increased remarkably due to the increased surface area and decreased crystallinity and degree of polymerization of cellulose. To further expand the application range of this method, we investigate the influences of ultrasonic pretreatment on bio-oil yield from real and complex biomass in this work. The cornstalk, one of the main agricultural wastes, is selected as experimental feedstock. To the best of our knowledge, so far no related reports can be found on using ultrasonic pretreatment to enhance the yield of bio-oil obtained from the cornstalk. The objective of this work is to study the feasibility of hydrothermal liquefaction of cornstalk by ultrasonic pretreatment to improve the yield of bio-oil. The influences of ultrasonic pretreatment on the physicochemical properties of cornstalks, the yields of bio-oil, and the chemical compositions of bio-oil are explored, respectively.

■ MATERIALS AND METHODS

Materials. The fresh and air-dried cornstalk was obtained from Shandong province, China. The raw material was subjected to a series of treatments: washing using deionized water to remove dirt, drying in an oven at 100 °C for 4 h, and crushing with a compact pulverizer. The cornstalk powder was passed through a sieve with a 100 mesh screen and then stored in a valve bag. The chemical components of cornstalk

were determined according to the reported methods.[20] The contents of ash were measured according to ASTM standards.[21] The elemental compositions of cornstalk were performed in terms of JY/T017-1996 on a Vario EL III elemental analyzer (Elementar, Germany). The high heat value (HHV) of cornstalk was calculated according to Dulong's equation:

$$HHV\ (MJ/kg) = 0.3383C + 1.422(H - O/8) \qquad (1)$$

The analysis results show that the dried cornstalk involves 37.36% cellulose, 29.54% hemicellulose, 18.16% lignin, and 3.34% ash. The C, H, O, and N contents are 47.80, 6.01, 45.18, and 1.02%, respectively. The HHV of the cornstalk is 16.69 MJ/kg.

Ultrasonic Pretreatment. The cornstalk powder was pretreated by an ultrasound generation system (1200Y, Bi Long Inc., China), which involves an ultrasonic generator of 20 kHz frequency and a Ti-6 Al-4 V (a kind of titanium alloy) cylindrical horn with a probe (Φ = 15 mm). Pretreatment was carried out in a 60 mL glass beaker equipped with a water bath, which can control the system temperature to maintain a constant 30 °C. In each run, 5 g of the cornstalk and 50 mL of deionized water (pH 6.8) were put in the glass beaker and mixed adequately before pretreatment. The ultrasonic generator has a maximum power output of 1200 W, and the power used was set at 5% (60 W) in pretreated experiments. It needs to be noted that the actual ultrasonic power is lower due to the energy loss caused by the reflection and refraction of ultrasound waves in the water medium. The actual energy output power is measured by calorimetry and calculation based on eq 2[22−25]

$$actual\ power\ (W) = m \times C_p \times (dT/dt) \qquad (2)$$

where m is the mass of water, C_p is the heat capacity of water, and dT/dt is the temperature increase per second of water.

The result shows that the actual energy output power is approximately 9.29 W.

Preparation of Bio-oil. The hydrothermal conversion of cornstalk to bio-oil was carried out in a 450 mL stainless steel reactor (Nantong Huaxing Petroleum Instrument Co., Ltd., China) with a pressure gauge and temperature controller. In a typical run, the sonicated cornstalk slurry was directly loaded into the reactor without filtration and drying. The reactor was sealed and then evacuated using a vacuum pump to get rid of the oxygen. At the heating rates of 6−10 °C/min, the reactor was heated to the desired temperature and kept for a desired holding time. Then the high-temperature reactor was quenched immediately by tap water for roughly 10 min until the reactor temperature decreased to 25 °C. A sufficient time was allowed to achieve phase equilibria of gas, liquid, and solid products before the reactor was opened. Afterward, the gaseous product was vented and not collected because this work mainly focuses on the liquid products, but the effects of ultrasonic pretreatment on the yield and carbon balance of gaseous product were also considered by differences in the following. The liquid and solid products in the reactor were transferred into a beaker together, and then they were separated by reduced filtration. The water in the filtrate was removed by a rotary evaporator at 40 °C, and the water-soluble oil (WSO) was obtained. The solid product was extracted by acetone at least three times until the washing liquor became colorless. The acetone in the extract liquor was removed by using a blowing nitrogen method at ambient temperature, and the leftover was designated heavy oil (HO). The HO and WSO are collectively called bio-oil. The residue extracted was dried in an oven at 105 °C for 2 h and designated solid residue (SR). Separation and preparation procedures of products liquefied from cornstalk in hot-compressed water are shown in Figure 1. The yields of HO, WSO, and SR are calculated by dividing the mass of products by the mass of dry cornstalk. The yield of the gas is calculated by differences: gas yield (wt %) = 100 (wt %) − HO yield (wt %) − WSO yield (wt %) − SR yield (wt %)

The unsonicated cornstalks were also liquefied in accordance with the mix proportion of 5 g of sample and 50 mL of deionized water as control groups. All experiments were repeated three times, and the relative deviations were within ±5%.

Analysis. The gas chromatography−mass spectrometry (GC-MS) analyses of bio-oils (HO and WSO) were conducted on a GC-MS spectrometer (Agilent 7890A/5975C, USA). All concentrations of the bio-oil samples were selected as 15 mg/mL. The solvents used for HO and WSO samples were acetone (chromatographically pure) and methanol (chromatographically pure), respectively. A column of HP-5MS (5% phenyl methyl siloxane, 30 m × 0.25 mm × 0.25 μm) was used in the analyses. The oven temperature was set programmatically: isothermal at 60 °C for 4 min, then temperature rise at a rate of 5 °C/min to 300 °C, and a hold for 8 min at the final temperature. The compounds were identified with the help of NIST11.

To investigate the effects of the ultrasonic pretreatment on the structure, infrared signatures, crystallinity, and surface area of cornstalk, SEM, FT-IR, XRD, and BET surface analyses were conducted, respectively. For sonicated cornstalks, the freeze-drying of sonicated cornstalk slurries was first carried out on a vacuum freeze-dryer (FreeZone Stoppering Tray Dryer, Labconco) to preserve their original structures as much as possible. After dried cornstalk samples were obtained, they were stored in desiccators at room temperature. Scanning electron microscopy (SEM, Hitachi S-4800) was used to observe the surface structures of the sonicated and unsonicated cornstalks. The effects of ultrasonic pretreatment on the infrared signatures of the cornstalks were analyzed on a Spectrum 100 Fourier transform infrared spectrophotometer (FT-IR, Perkin-Elmer Inc., USA) using a KBr sheet containing 2% of samples. The BET surface areas of the sonicated and unsonicated cornstalks were determined on NOVA2200e surface area analyzer (Quantachrome, USA). The crystallinities of the sonicated and unsonicated cornstalks were measured on a model D/max-2200/PC X-ray diffractometer (XRD, Rigaku Co., Japan). The samples were irradiated at 6−40° with a scan rate of 4°/min. The crystallinity index (CrI) was calculated with the diffraction intensities on the basis of formula 3[26]

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \tag{3}$$

where I_{002} is the intensity of crystalline portion (2θ is about 22.5°) and I_{am} is the intensity for amorphous portion (2θ is about 16.8°).

The elemental compositions of the sonicated cornstalk, HO, WSO, and SR were also analyzed by using an Elementar Vario EL III analyzer. Their HHVs were calculated according to eq 1.

■ RESULTS AND DISCUSSION

Characterization of the Sonicated and Unsonicated Cornstalks. After ultrasonic pretreatment, the appearance of the cornstalk greatly changed and the volume of the cornstalk in the water was significantly increased. Figure 2 shows pictures
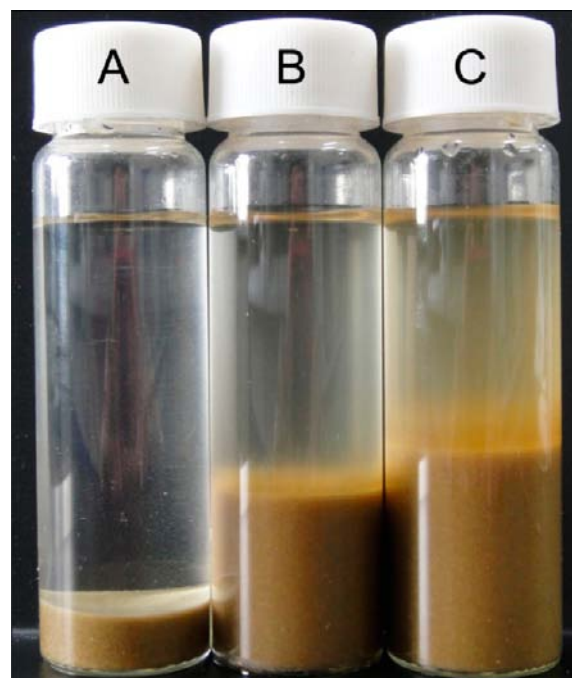

Figure 2. Pictures of cornstalks in water before and after ultrasonic pretreatment: (A) unsonicated; (B) 20 min; (C) 40 min.

of the sonicated and unsonicated cornstalks in the water pretreated under the same conditions (such as loading of 5 g material/50 mL water and ultrasound power of 60 W) except sonication time. The sonicated cornstalks were well dispersed in the water and formed stable suspensions. The effect of ultrasonic pretreatment on the dispersion of cornstalk in water can be amplified with increasing sonication time. This indicates that ultrasonic pretreatment is conducive to the enhancement of the accessibility of the cornstalk. SEM images of the sonicated and unsonicated cornstalks are shown in Figure 3. The surface structures of the cornstalks were greatly changed by ultrasonic pretreatment. Compared to the smooth surface of raw cornstalk, the surfaces of sonicated cornstalks were seriously eroded and showed many etch pits. Especially when the sonication time was prolonged to 40 min, a large hole with a diameter of about 5−6 μm was observed. The ultrasonic pretreatment significantly damaged the surface structure of the cornstalk and increased the pore size, which may be caused by the cavitation taking place near the surface of the cornstalk. The collapse of the bubbles can generate enough force to damage the surface of the cornstalk, and this effect is called the "mechanoacoustic effect".[27]
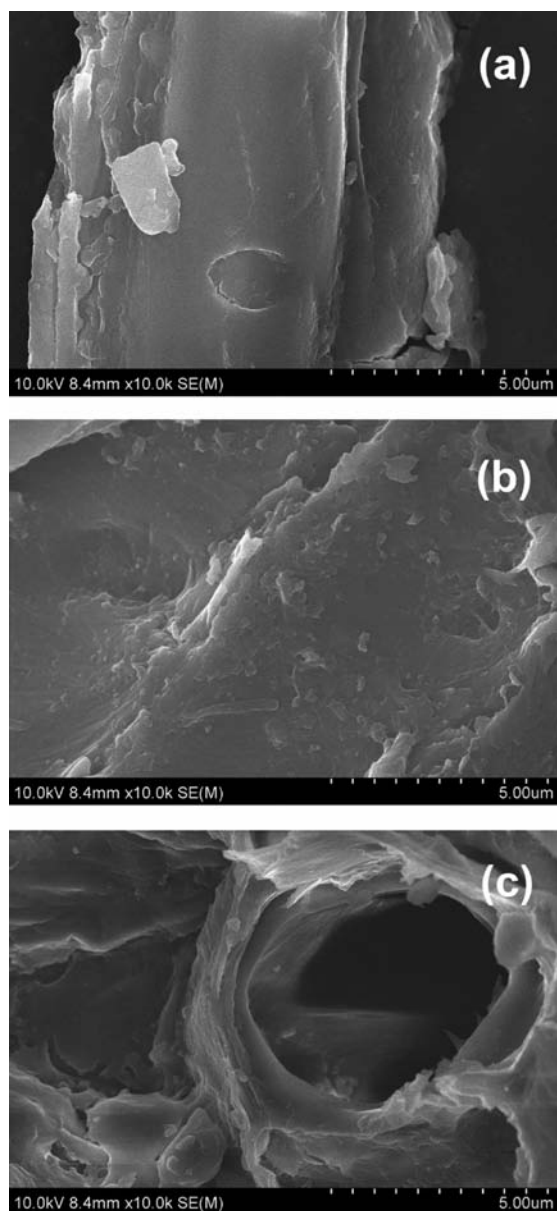
Figure 3. SEM images of unsonicated and sonicated cornstalks: (a) unsonicated; (b) 20 min; (c) 40 min.

Figure 4. FT-IR spectra of the sonicated and unsonicated cornstalks: (a) unsonicated; (b) 20 min; (c) 40 min.

In addition, ultrasound also generates an important sonochemical effect by the formation of radicals, which may influence the physicochemical property of the cornstalk. Thus, FT-IR analyses of the sonicated and unsonicated cornstalks were performed. As seen in Figure 4, ultrasonic pretreatment affects the infrared signatures of the cornstalks, and some changes are found. For instance, the intensity ratios of the peaks at 1516 and 1610 cm^{-1} in the sonicated and unsonicated cornstalks increase; this may be caused by the demethylation of the syringyl structure of lignin.[28] The intensities of the peaks at 1156 and 1157 cm^{-1} increase after ultrasonic pretreatments, which are associated with the increased contents of the guaiacyl group in sonicated cornstalks.[29] This indicates that ultrasonic pretreatment decreases syringyl structure units but increases guaiacyl structure units in the lignin. The subunits and firm network of lignin are partly destroyed, which allows more cellulose and hemicellulose to be exposed. This can be proven by the changes of peak intensities of cellulose and hemicellulose
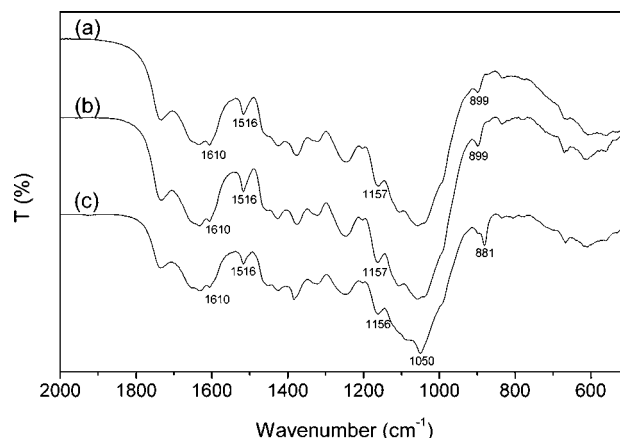
in cornstalks. The sonicated cornstalks have more strong absorption peaks at 1050 cm^{-1}, which is the typical signal of the C−O−C stretching of glucan and xylan.[30,31] Additionally, the increases of absorption peaks at 899 and 881 cm^{-1} originating from the β-glucosidic linkages between the sugar units in cellulose and hemicellulose indicate that ultrasonic pretreatment results in more exposure of the interior cellulose and hemicellulose in the cornstalk. In the ultrasound processing, the water will generate oxidants (such as hydrogen peroxide and ozone) by a series of free radical reactions.[32] The integration of the attack of the oxidants on lignin with the mechanoacoustic effect may ultimately lead to the partial decomposition and erosion of lignin.

The surface areas of the sonicated and unsonicated cornstalks were measured by BET analysis, and the results show that ultrasonic pretreatment increases the surface areas of cornstalks remarkably from 2.84 m^2/g (unsonicated) to 5.09 m^2/g (20 min) and 5.87 m^2/g (40 min). A larger surface area of cornstalk trends to have a faster degradation reaction rate in the hot-compressed water. The CrIs of the sonicated and unsonicated cornstalks were also calculated to measure the effects of the ultrasonic pretreatment on the cornstalks. The results indicate that the CrIs decrease from 50.87% (unsonicated) to 46.19% (20 min) and 46.43% (40 min). This may be attributed to the cleavages of intermolecular hydrogen bonds in the crystalline regions caused by ultrasound.

Effect of Temperature on Bio-oil Yield. The reaction temperature is one of the most important parameters for the conversion of biomass to bio-oil in hot-compressed water. Thus, the effect of different temperatures (260, 280, 300, 320, and 340 °C) on the yields of products was investigated with a residence time of 0 min. Figure 5 shows the yields of products obtained from liquefaction of unsonicated and sonicated cornstalks. For raw cornstalk feedstock, the yield of SR decreases from 35.2 to 18.8% with increasing temperature from 260 to 300 °C and then increases to 20.6% as the temperature further increases to 340 °C. For sonicated cornstalks, the SR yields have similar development tendencies as the increasing temperature, but they are lower than that of the unsonicated cornstalk at the whole temperature range. The lowest SR yield of 15.0% was obtained at 300 °C for the sonicated cornstalk with a pretreatment time of 40 min. The decreased yield of SR may be attributed to the large surface area and damaged lignin structure of the sonicated cornstalks.
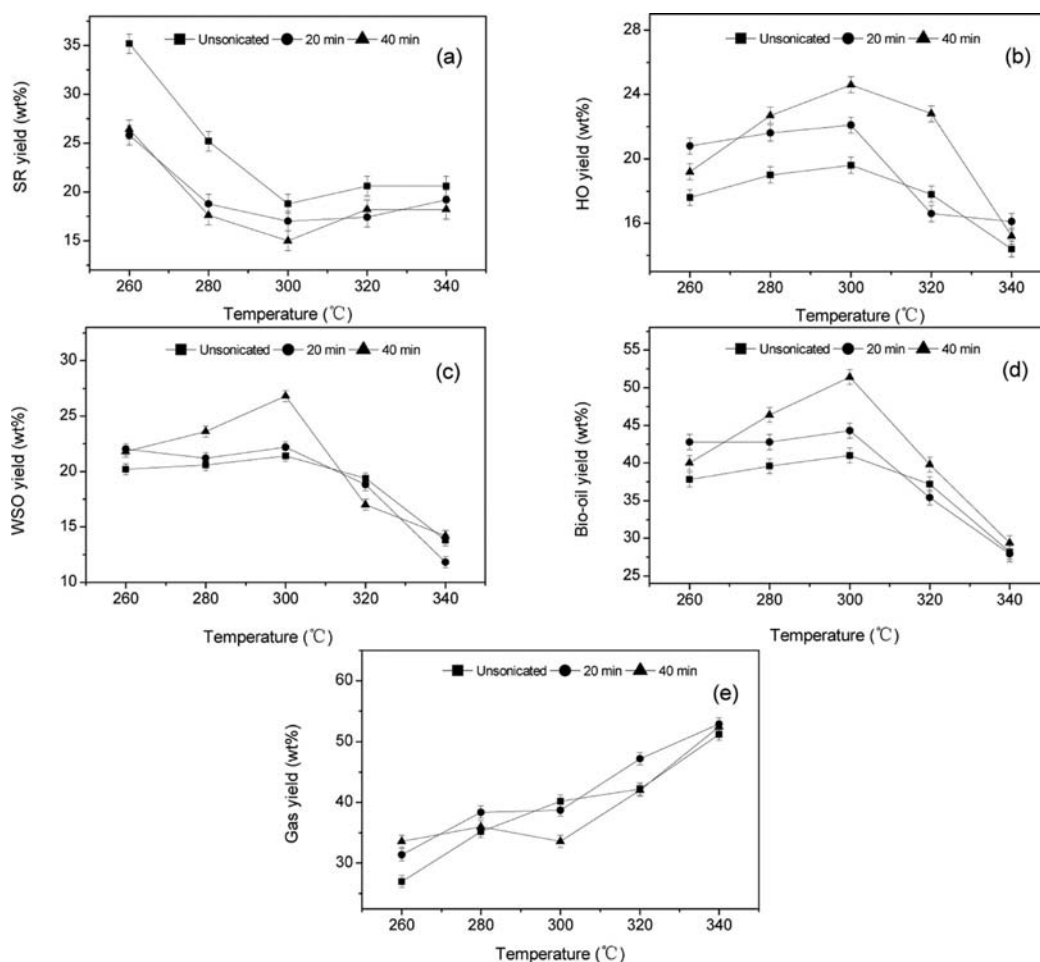
Figure 5. Effect of temperature on the yields of products derived from liquefaction of unsonicated and sonicated cornstalks: (a) SR yield; (b) HO yield; (c) WSO yield; (d) bio-oil yield; (e) gas yield.

The yields of HO and WSO produced from the liquefactions of cornstalks at different temperatures are shown in Figure 5b,c. For the sonicated and unsonicated cornstalks, the temperature has a significant influence on the yields of HO and WSO: initially the yields of HO and WSO increase as the temperature increases to 300 °C, and then they immediately decrease with further increasing temperature. This may be because the elevated temperature promotes free radical reactions between biomass and water and results in increments of bio-oil yields.[33,34] However, an excessively high temperature will exacerbate the secondary and tertiary decompositions of bio-oil to gas and SR and lead to decreases of bio-oil yields and increases of gas and SR yields, as shown in Figure 5a,e.

The highest yields of HO and WSO were obtained at 300 °C, being 19.6% (HO, unsonicated), 22.1% (HO, 20 min), 24.6% (HO, 40 min), 21.4% (WSO, unsonicated), 22.2% (WSO, 20 min), and 26.8% (WSO, 40 min). The sonicated cornstalks have higher HO and WSO yields than unsonicated cornstalk. This indicates that ultrasonic pretreatment is favorable to increase the conversion of cornstalk to bio-oil in hot-compressed water medium. As seen in Figure 5d, the maximum bio-oil yield increases from 41% (unsonicated) to 44.3% (20 min) and 51.4% (40 min). The increases of the bio-oil yields could be attributed to the changes in structure of cornstalks after ultrasonic pretreatment, such as the lower crystallinities and the greater exposures of cellulose and hemicellulose, which

are more accessible to conversion of cornstalks and increase bio-oil yields.

Effect of Residence Time on Bio-oil Yield. The liquefaction experiments of unsonicated and sonicated cornstalks were conducted at 300 °C for different residence times (0, 10, 20, 30, and 40 min). Figure 6 presents the yields of products including SR, HO, WSO, bio-oil, and gas. The yields of SR for unsonicated cornstalk increase from 18.8% with 0 min of residence time to 23.6% with 40 min of residence time. The yields of SRs for sonicated cornstalks also increase with increasing residence time. In comparison, sonicated cornstalks have lower SR yields and higher conversions of cornstalks (defined as 100% − SR %). This indicates the effects of ultrasonic pretreatment on the conversion of cornstalks have always been there with increasing residence time from 0 to 40 min. Longer residence time results in higher SR and gas yields and lower HO, WSO, and bio-oil yields. As shown in Figure 6, the yields of HO, WSO, and bio-oil continuously reduce, whereas the yields of SR and gas increase with the increasing residence time. These results could be attributed to the decomposition and polymerization of bio-oil to SR and gas with increasing residence time.

The effects of ultrasonic pretreatment on the yields of HO, WSO, and bio-oil are remarkable within the residence times of 0−30 min. The sonicated cornstalks have higher yields of HO, WSO, and bio-oil than the unsonicataed cornstalk. Good accessibilities and exposures of cellulose and hemicellulose
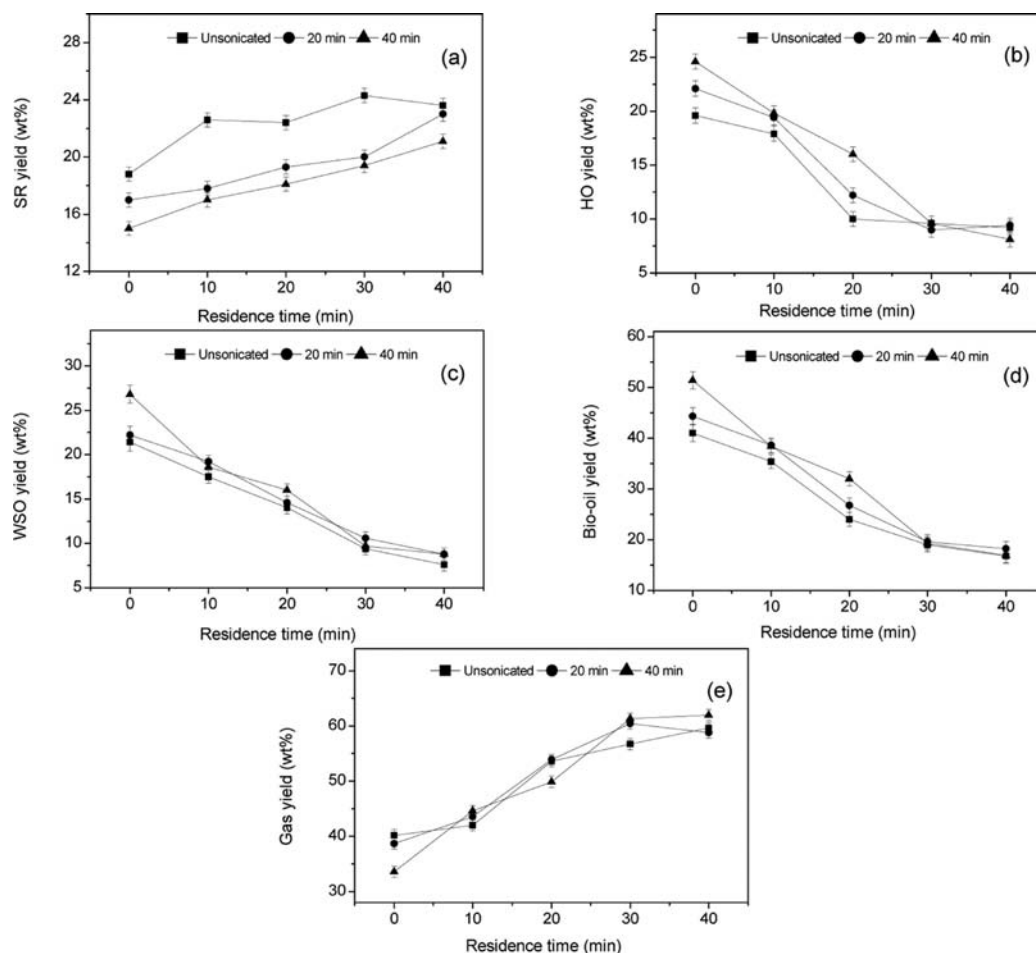
Figure 6. Effect of residence time on the yields of products derived from liquefaction of unsonicated and sonicated cornstalks: (a) SR yield; (b) HO yield; (c) WSO yield; (d) bio-oil yield; (e) gas yield.

improve the degradation rates and the conversions of sonicated cornstalks to bio-oils. However, when the residence time reaches 40 min, the effects of ultrasonic pretreatment on the bio-oil yields are not obvious. This may be because the decomposition and polymerization of bio-oil are more dominant for longer residence time compared with the increases of hydrolysis rate of cornstalk caused by ultrasonic pretreatment. Thus, the residence time of 0 min is suitable for the increases of bio-oil yields and reductions of SR and gas yields.

Carbon Balance and Energy Recovery. To study carbon balance and energy recovery, elemental analyses of raw cornstalk feedstock and liquefied products prepared under optimum conditions (300 °C and 0 min of residence time) were performed. The elemental analysis results are presented in Table 1. The carbon balances are calculated on the basis of eq 4

$$\text{carbon balance (wt \%)} = \frac{C_i \times Y_i}{C_T} \times 100\% \qquad (4)$$

where C_i is the carbon content of HO, WSO, and SR, respectively; Y_i is the yield of the HO, WSO, and SR, respectively; and C_T is the carbon content of raw cornstalk. It needs to be mentioned that the carbon balances of the products from sonicated cornstalks are also calculated on the basis of the raw cornstalk. The differences of elemental compositions between unsonicated and sonicated cornstalks are small and

Table 1. Elemental Analysis and HHV of Products Obtained from the Liquefaction of Cornstalks at 300 °C for 0 min of Residence Time

sample[a]	C (wt %)	H (wt %)	N (wt %)	O (wt %)[b]	HHV (MJ/kg)
cornstalk	47.80	6.01	1.02	45.18	16.69
HO-0	67.88	6.61	1.92	23.58	28.18
HO-20	67.10	6.58	1.83	24.49	27.97
HO-40	64.57	6.66	1.90	26.87	27.40
WSO-0	53.70	5.79	1.85	38.67	19.52
WSO-20	53.84	6.24	1.84	38.08	20.32
WSO-40	54.16	6.61	1.88	37.35	21.08
SR-0	65.33	5.98	1.77	26.93	25.82
SR-20	51.78	5.88	1.75	40.59	18.66
SR-40	47.80	5.96	1.83	44.41	16.75

[a]Cornstalk, unsonicated cornstalk; HO-0, HO from unsonicated cornstalk; HO-20, HO from 20 min sonicated cornstalk; HO-40, HO from 40 min sonicated cornstalk; WSO-0, WSO from unsonicated cornstalk; WSO-20, WSO from 20 min sonicated cornstalk; WSO-40, WSO from 40 min sonicated cornstalk; SR-0, SR from unsonicated cornstalk; SR-20, SR from 20 min sonicated cornstalk; SR-40, SR from 40 min sonicated cornstalk. [b]By differences.

negligible when no separation or filtration is performed before liquefaction of the sonicated cornstalk slurries.

The results of carbon balance listed in Table 1 indicate that ultrasonic pretreatment increases the carbon conversions of

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cornstalks to HOs and WSOs. The carbon recovery of bio-oil improves from 51.87% (unsonicated) to 56.03% (20 min) and 63.605% (40 min). The increases of carbon recovery of bio-oil are mainly attributed to the increased bio-oil yields of sonicated cornstalks. Moreover, ultrasonic pretreatment decreases the carbon recovery of SR from 25.69% (unsonicated) to 18.42% (20 min) and 15.00% (40 min). The carbon recoveries of gas are obtained by the differences. Ultrasonic pretreatment seems to increase the carbon transfer to gas. Even so, the increase of carbon recovery of bio-oil is more predominant compared with that of gas.

Energy balances about ultrasonic pretreatment and bio-oil preparation were estimated on the basis of the HHVs of bio-oil using energy efficiency (Eff), as shown in eq 5

$$
\begin{aligned}
\text{Eff (\%)} \ &= \frac{E_{\text{bio-oil}} - (E_{\text{pretreatment}} + E_{\text{heating}})}{E_{\text{pretreatment}} + E_{\text{heating}}} \times 100\% \\
&= \left[\frac{m_{\text{b}}(Y_{\text{HO}}HHV_{\text{HO}} + Y_{\text{WSO}}HHV_{\text{WSO}})}{Pt + (m_{\text{b}}C_{pb}\Delta T + m_{\text{w}}C_{pw}\Delta T)(1 - R_{\text{h}})} \right. \\
&\quad \left. - 1 \right] \times 100\%
\end{aligned}
$$

(5)

where $E_{\text{bio-oil}}$ is the energy of the obtained bio-oil (J); $E_{\text{pretreatment}}$ and E_{heating} are the energy consumptions in the processes of ultrasonic pretreatment and heating (J), respectively; m_{b} and m_{w} are the masses of cornstalk and water (g), respectively; Y_{HO} and Y_{WSO} are the yields of HO and WSO, respectively; HHV_{HO} and HHV_{WSO} are the heat values of HO and WSO, respectively; P is the actual ultrasonic power (W); t is the sonication time (s); C_{pb} (1.25 J/g/k) and C_{pw} (4.18 J/g/K) are the specific heats of cornstalk and water, respectively; ΔT is the temperature difference (275 L); and R_{h} is the heat recovery efficiency of the liquefaction system (0.5).

Table 2 shows the results of energy balances for the liquefaction of cornstalks in hot-compressed water. The energy

Table 2. Carbon Balance and Energy Recovery for the Liquefaction of Cornstalks in Hot-Compressed Water

sample	carbon balance (wt %)				Eff (%)
	HO	WSO	SR	gas[a]	
unsonicated	27.83	24.04	25.69	22.43	63.87
20 min	31.02	25.01	18.42	25.56	31.20
40 min	33.23	30.37	15.00	21.40	19.38

[a]By differences.

efficiencies are 63.87% for the unsonicated cornstalk, 31.20% for 20 min sonicated cornstalk, and 19.38% for 40 min sonicated cornstalk. The unsonicated cornstalk has relatively higher energy efficiency than sonicated cornstalks due to no energy consumption in the step of ultrasonic pretreatment. However, the sonicated cornstalks also have positive energy balances, which means that ultrasonic pretreatment did not cause a net energy loss in the total process of bio-oil preparation. The energy consumption of ultrasonic pretreatment depends largely on the ultrasonic power output, the ultrasonic frequency, the sonicated time, and the loading of cornstalk. In addition, the geometry of ultrasonic reactor, batch versus flow, and method of ultrasound delivery will influence

energy the efficiency and efficacy of the pretreatment as well.[27,35] Therefore, the energy efficiency of ultrasonic pretreatment can be optimized by studying operating parameters and adjusting the ultrasonic device.

GC-MS Analysis of Bio-oil. To investigate the effects of ultrasonic pretreatment on the chemical compositions of bio-oils, GC-MS analyses of HO and WSO produced from the liquefactions of unsonicated and sonicated cornstalks at 300 °C for 0 min of residence time were performed. The major identified compounds and their relative contents from HO and WSO are listed in Tables 3 and 4. The analysis results

Table 3. Major Identified Compounds and Relative Contents from HOs Obtained from the Liquefaction of Cornstalks at 300 °C and a Residence Time of 0 min

RT (min)	compound	content (%)		
		unsonicated	20 min	40 min
8.62	phenol	6.03	8.43	7.11
9.98	2-cyclopenten-1-one, 2-hydroxy-3-methyl-	1.65		
11.61	p-cresol	1.73	1.91	1.84
11.94	phenol, 2-methoxy-	3.87	4.88	4.94
12.67	4(1H)-pyridone	1.56		
14.42	phenol, 4-ethyl-	14.52	17.47	14.88
17.13	naphthalene, 2,6-bis(1,1-dimethylethyl)-	2.31	3.00	
17.59	phenol, 4-ethyl-2-methoxy-	10.18	12.01	10.18
19.58	phenol, 2,6-dimethoxy-	6.12	8.53	8.42
20.90	vanillin	2.06	2.08	1.76
21.07	ethanone, 1-(2-hydroxyphenyl)-	2.25		
22.07	1,2,4-trimethoxybenzene		2.82	3.25
22.26	eugenol	1.80	1.83	2.09
23.12	ethanone, 1-(4-hydroxy-3-methoxyphenyl)-			2.10
24.00	5-tert-butylpyrogallol	2.61		
26.01	2,4-hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester, (Z,E)-		1.98	
27.39	2-naphthalenol, 3-methoxy-	1.45		2.05
28.17	2-propenoic acid, 3-(4-hydroxy-3-methoxyphenyl)-		1.87	
28.68	phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.69		1.77
28.80	ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	4.47	5.63	5.38
40.77	9-octadecenamide, (Z)-	3.03	4.01	7.95
41.57	phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	1.68		1.96
51.80	vitamin E		1.81	2.33

demonstrate that HO mainly consists of phenols, ketones, aldehydes, and acids, such as 4-ethylphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol, phenol, 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone, 1-(2-hydroxyphenyl)ethanone, vanillin, and 3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid. Phenols are the main compounds in the HO for both unsonicated and sonicated cornstalks, which are mainly the products of decomposition of lignin and derived partly from cellulose.[36,37] Nonetheless, the ultrasonic pretreatment has a tendency to increase the contents of phenols in the HO. The total content of phenols in HO for unsonicated cornstalk is 47.35%, whereas those for sonicated cornstalks are 54.96% (20 min) and 55.74% (40 min). This may be because the erosion of the lignin network structure and the partial decomposition of

Table 4. Major Identified Compounds and Relative Contents from WSOs Obtained from the Liquefaction of Cornstalks at 300 °C and a Residence Time of 0 min

RT (min)	compound	content (%)		
		unsonicated	20 min	40 min
10.01	2-cyclopenten-1-one, 2-hydroxy-3-methyl-		7.63	8.05
11.46	pentanoic acid, 4-oxo-			1.02
13.47	pyridine, 3-trimethylsiloxy-	5.90		
13.86	2-amino-6-methylbenzoic acid			1.56
14.42	phenol, 4-ethyl-	3.61		
15.04	2-hexene, (E)-	3.05	4.62	3.69
15.14	2-hexene, 2-methoxy-	1.83		
15.44	catechol	3.98	3.97	3.32
16.68	2-cyclohexen-1-one, 4-(1-methylethyl)-			1.75
17.13	1,2-benzenediol, 3-methoxy-		6.41	5.82
17.59	phenol, 4-ethyl-2-methoxy-		1.49	1.97
18.77	3-cyclohexen-1-one, 2-isopropyl-5-methyl-			0.92
19.60	phenol, 2,6-dimethoxy-	19.27	23.48	25.24
20.93	vanillin	1.04		
22.07	benzenecarbodithioic acid, methyl ester			1.51
23.12	apocynin	1.16	2.25	1.46
28.80	ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	11.43	18.18	17.70
31.24	phenol, 3,5-dimethoxy-		1.82	2.44
32.95	2,5-cyclohexadien-1-one, 3,5-dihydroxy-4,4-dimethyl-	1.16		
33.17	5-isopropylidene-3,3-dimethyldihydrofuran-2-one	3.00	3.50	4.46
41.55	phenol, 2,2′-methylenebis[6-(1,1-dimethylethyl)-4-methyl-			1.56

lignin in the process of ultrasonic pretreatment facilitate the conversion of lignin to phenols.

Table 4 displays the major identified compounds and their relative contents from WSO. WSO is mainly composed of 2,6-dimethoxyphenol, 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone, catechol, (E)-2-hexene, and 5-isopropylidene-3,3-dimethyldihydrofuran-2-one, etc. Similar to HO, ultrasonic pretreatment increases the relative contents of phenols, and some new compounds are found, such as 2-hydroxy-3-methyl-2-cyclopenten-1-one, 4-oxopentanoic acid, 3-methoxy-1,2-benzenediol, 3,5-dimethoxyphenol, and benzenecarbodithioic acid methyl ester. The amelioration of mass and heat transfer and the changes of chemical compostions of sonicated cornstalks may account for the differences of identified compounds and contents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total ion chromatograms (TIC) of HO and WSO obtained from liquefaction of cornstalks at 300 °C for 0 min of residence time. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

■ ABBREVIATIONS USED

HO, heavy oil; WSO, water-soluble oil; SR, solid residue; GC-MS, gas chromatography−mass spectrometry; SEM, scanning electron microcopy; FT-IR, Fourier transform infrared spectrophotometer; XRD, X-ray diffractometer; CrI, crystallinity index; HHV, high heat value; Eff, energy efficiency

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