

Comparative study of conventional and microwave-assisted liquefaction of corn stover in ethylene glycol

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ABSTRACT

A comparative study on conventional and microwave-assisted liquefaction of corn stover has been carried out using ethylene glycol (EG) as liqueficient and sulfuric acid as catalyst. Microwave dramatically increased the liquefaction extent and rate compared to conventional heating. The liquefied products and residues in both methods have been investigated using gel permeation chromatography (GPC), Fourier transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The GPC results show that the molecular weight of liquefied products with conventional heating is significantly greater than those of microwave-assisted liquefaction. The FTIR spectra indicate that there are significant differences in the hydroxyl and carbonyl group contents in the liquefied products with the two methods. The residue from microwave-assisted liquefaction mainly consisted of mineral matter. Many granules appeared on the surface of microwave liquefied residue according to SEM observation.

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1. Introduction

The utilization of plant material as a supplemental source for liquid fuel and chemical feedstock is a promising approach for minimizing our dependence on fossil energy (Wang and Huffman, 1981). Liquefaction of biomass has been attracting increasing attention. At elevated temperatures and the presence of polyhydric alcohol and acids, lignocellulose resource is converted into multifunctional polyols, which could be used as raw material for polyurethane production (Kurimoto et al., 2001). Most reports concerning polyhydric alcohol liquefaction focused on the use of external heating as the thermal resource (Lee et al., 2000; Kurimoto et al., 2001; Ge et al., 2000; Hassan and Shukry, 2008). The main limitations of the conventional heating are time-consuming and low liquefaction rate.

Microwave irradiation is an alternative method to conventional heating. Compared with conduction/convection heating, which is based on interfacial heat transfer, microwave uses the ability of direct heating of the target object due to applied electromagnetic field. Microwave heating is volumetric and rapid (Hoz et al., 2005). The application of microwave irradiation to liquefy wood into polyols was reported recently (Kržan and Kunaver, 2006; Kržan and Žagar, 2009). Based on the fact that there are abundant crop residue and limited forestry resource in China, significant efforts should be

taken to utilize crop residue to fulfill large-scale industrial production of bio-energy (Li et al., 2010). In the present study, microwave irradiation was applied in corn stover liquefaction using ethylene glycol (EG) as solvent and sulfuric acid as catalyst. Characterization of the liquefied products and residues was carried out to differentiate the microwave-assisted liquefaction from conventional liquefaction

2. Materials and methods

2.1. Materials and chemicals

Corn stover used in the experiments was dried and grounded with a blade-mill (FW135 Medicine Mill, China) and then sieved through a 40-mesh screen. The reagents used were chemical grade (Beijing Chemical Plant, China).

2.2. Liquefaction procedure

Liquefactions were carried out in a Milestone microwave laboratory system equipped with 100 mL sealed teflon reaction vessels and with an internal temperature sensor. Samples were irradiated from 5 to 30 min under 600 W as starting microwave power. The sample temperature is controlled at 160 °C. The reaction mixture consisted of 6.0 g corn stover powder, 20.0 g liquefaction reagent EG and 0.70 g catalyst sulfuric acid and was mixed with magnetic stirring during liquefaction. After liquefaction for a preset time (5–30 min), the vessels were allowed to cool at room temperature before opening.

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The 7.5 g corn stover powder, 25.0 g EG and 0.875 g sulfuric acid were mixed thoroughly before put in a 100 mL three-neck flask for conventional liquefaction. The flask was placed in an oil bath (160 °C) with refluxing and stirring for 30–120 min.

2.3. Measurement of liquefaction extent (Yao et al., 1994)

After cooling, the product was diluted with 80% 1,4-dioxane (dioxane:water=80:20, v:v). The diluted resultant was filtered to separate the residue and filtrate. The residue was washed with 80% 1,4-dioxane, dried at 105 °C for 12 h in an oven and then weighed. The residue content was defined as the percent of the dry weight of dioxane insoluble substance to the total raw corn stover material charged. It has been usually used as an index of the liquefaction extent.

$$\text{Residue content (\%)} = \frac{\text{Residue weight (g)}}{\text{Weight of raw material (g)}} \times 100$$

2.4. Analysis of average molecular weight

GPC was used to determine the molecular weight of the liquefied products using a Waters1515 gel permeation chromatograph equipped with a differential refractometer R401 detector. Tetrahydrofuran was used as the mobile phase at the flow rate of 1.5 mL/min. The concentration of the samples was 0.5 wt% in the THF solution and the injected amount was 100 mL. The molecular weights of the samples were calibrated with polystyrene standards.

2.5. FTIR analysis

Fourier transform infrared (FTIR) was used to study the components in CS liquefied products. The filtrate from residue content was condensed and freeze-dried for FTIR analysis on a Perkinelmer 400 spectrometer. Attenuated total reflection measurements were conducted for the samples.

2.6. XRD analysis

The X-ray diffraction patterns of the samples were measured with a XD-2 X-ray diffractometer (Beijing Purkinje General Instrument Co. Ltd., China). Absorbent cotton, raw corn stover, and corn stover residues from conventional liquefaction (120 min)/microwave-assisted liquefaction (20 min) were pulverized using a carnelian mortar. XRD analysis was performed at 36 kV and 20 mA using nickel-filtered Cu-K (wavelength 1.5405 Å) radiation. The scan was done from 8° to 40° with a scanning speed of 0.25°/min and sampling interval of 0.02°.

Jade 5.0 was used for the peak fitting and phase determination. The biomass crystallinity index (CrI) was defined as the percentage of crystalline material in the biomass and was calculated according to the empirical method proposed by Segal et al. (1959):

$$\text{CrI} = \left(\frac{I_{002} - I_{\text{am}}}{I_{002}} \right) \times 100$$

where CrI is the crystallinity index, I_{002} is the maximum intensity of the 002 peak at $2\theta = 22.5^\circ$, and I_{am} is the intensity at $2\theta = 18.0^\circ$.

2.7. Scanning electron microscopy

A Hitachi S-3400 SEM instrument (15–20 kV accelerated voltage) was used to examine the morphology of raw samples and liquefied residue in order to compare the effect of different heating treatments. There are three samples: (1) raw corn stover; (2) conventional liquefaction residue (120 min). (3) microwave-assisted liquefaction residue (20 min). Specimens were prepared for SEM

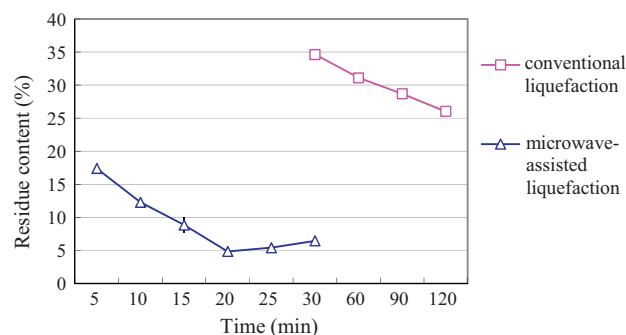


Fig. 1. Residue content of conventional and microwave-assisted liquefaction.

inspection by sticking a sample on carbon glue and allowing to be Pt-plated.

2.8. Statistical analysis

The one-way ANOVA test was used to calculate the significance of the comparison in the residue contents and in the molecular weight data. The analysis results were compared using Duncan's significant difference test. The p -values < 0.05 are considered significant.

3. Results and discussion

3.1. Liquefaction of corn stover with conventional and microwave-assisted heating

The residue content of liquefied corn stover as a function of liquefaction time is shown in Fig. 1 for conventional and microwave-assisted heating. The residue content with microwave liquefaction decreased rapidly when the heating time increases from 5 min to 20 min. When the reaction time is extended further, black pieces of insoluble content appeared in the residue, resulting in a slight increase in the residue content. This could be attributed to the lignin repolymerization reaction as reported (Rezzoug and Capart, 2002). Accordingly, 20 min is optimal reaction time for microwave assisted liquefaction with the minimal residue content of 4.85%. In contrast, the residue content reached 34.64% for conventional liquefaction at 30 min. At much extended reaction time, the residue content with conventional liquefaction is still very high, of 26.02% at 120 min, indicating incomplete liquefaction of corn stover. Compared with conventional liquefaction, microwave heating greatly accelerated the depolymerisation reaction of lignocellulosic components in corn stover as reported (Dřimalová et al., 2005). A different temperature regime caused by microwave heating is the main contributing factor to the acceleration of reaction observed (Bogdal et al., 2003). With microwave, heating is volumetric, leading to not only much rapid heating but also more uniform temperature distribution. Rapid and volumetric heating also induce significant structural change of corn stover at micro and cellular level as discussed later.

3.2. Molecular weight analysis for the liquefied product

Table 1 presents the number average (M_n) and the weight average (M_w) of molecular weights, as well as the molecular weight distribution (M_w/M_n) of liquefied products of conventional and microwave-assisted liquefaction.

With both methods, the molecular weights remained unchanged as reaction time extended (Table 1). It was also reported by others that the liquefaction time has little effect on the molecular weight and distribution (Lee et al., 2000; Chen and

Table 1
Molecular number-average (Mn), weight-average (Mw) and distributions (Mw/Mn) of liquefied product.

Sample name ^a	Mn	Mw	Mw/Mn
C-30	1020	2572	2.5
C-60	996	2444	2.5
C-90	1025	2560	2.5
C-120	990	2354	2.4
M-10	821	1405	1.7
M-20	820	1413	1.7
M-30	831	1413	1.7

^a C and M are the symbols of liquefied product with conventional and microwave-assisted liquefaction, respectively; numbers following indicate reaction time.

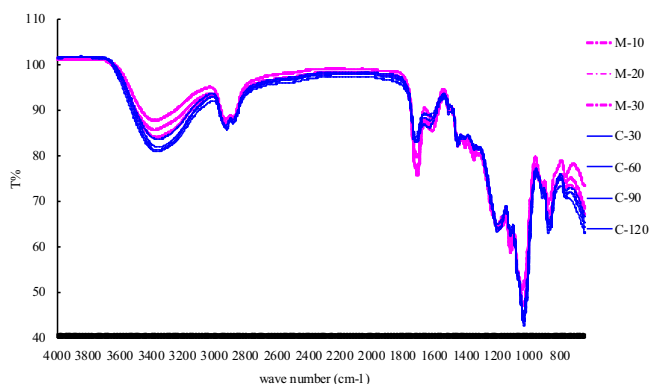


Fig. 2. FTIR of conventional and microwave-assisted liquefaction products (sample name was the same as in Table 1).

Lu, 2008). Prolonging the reaction time only increased the yield of liquefaction products as shown in Fig. 1.

However, it is interesting to note that the molecular weight of the liquefied products obtained by microwave-assisted liquefaction is considerably lower than those of the conventional method. It appears that microwave decomposed corn stover components into substances with relatively lower molecular weight than the conventional heating. This was also observed in the degradation of hyaluronan in comparison to microwave and conventional heating (Dřimalová et al., 2005). Furthermore, the molecular weight distributions for the microwave liquefied products are remarkably narrower than that for the conventional heating. This will greatly influence the utilization of the liquefied products.

3.3. FTIR analysis for the liquefied products

The FTIR spectra of liquefied product are shown in Fig. 2 for the two liquefaction methods. The assignment of typical bands (Bilba and Ouensanga, 1996; Pandey, 1999) and the relative absorbance are listed in Table 2. The relative intensities of bands at 3372 cm⁻¹ (O–H stretching), 2929 cm⁻¹ (C–H stretching), and 1036 cm⁻¹ (C–O stretching) are higher in conventional liquefied products, whereas the bands at 1713 cm⁻¹ (C=O stretching) are strong in microwave-assisted liquefied products. It indicates higher hydroxyl content

Table 2
FTIR absorbance and assignments of the liquefied products.

Wave number, cm ⁻¹	Absorbance							Assignment
	C-30	C-60	C-90	C-120	M-10	M-20	M-30	
3372	0.19	0.19	0.18	0.16	0.16	0.14	0.12	O–H stretching
2929	0.14	0.13	0.14	0.14	0.13	0.13	0.12	C–H stretching
1713	0.17	0.17	0.15	0.16	0.21	0.24	0.23	C=O stretching
1036	0.55	0.56	0.57	0.55	0.53	0.49	0.48	C–O stretching

Sample name was the same as in Table 1.

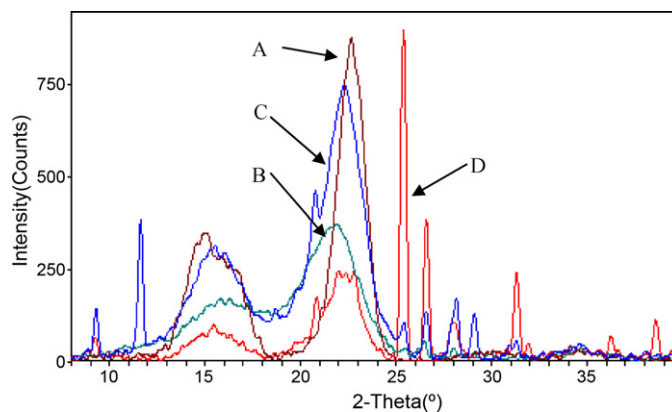


Fig. 3. X-ray diffractograms of raw corn stover and liquefied residue. Note: A, absorbent cotton; B, raw corn stover; C, conventional liquefaction residue (120 min); D, microwave-assisted liquefaction residue (20 min).

in conventional liquefied products but higher carbonyl content in microwave liquefied products. The oxidation of alcohols to carbonyl compounds is one of the fundamental transformations in organic chemistry (Sheldon and Kochi, 1981). It can be deduced that microwave induced more intensive oxidation of hydroxyl groups into carbonyl groups. The intensive C–H stretching (2929 cm⁻¹) indicated long chain hydrocarbon compounds in the products. The stronger absorption of conventional products at 2929 cm⁻¹ indicates longer carbon chain in the conventional products than that in the microwave products. This is in accordance with the molecular weight results discussed in the earlier Section 3.2.

All the characteristics of the liquefied products demonstrate that microwave induced more intense oxidation cleavage than conventional liquefaction.

3.4. Crystal components and crystallinity of residues

The crystallinity can be used to explain in detail the conversion progress for the large amounts of lattice cellulose in corn stover. We measured the XRD pattern of cellulose (absorbent cotton), raw corn stover, and corn stover residues after conventional and microwave-assisted liquefaction (Fig. 3). Careful assignment of all the observed X-ray diffraction peaks has been conducted using a diffraction peak-fitting program of Jade 5.0. Accordingly, the phase constituents contained in the residue are characterized in Table 3 and the CrI of cellulose have been determined.

Comparing the pattern of the four samples, the raw corn stover and conventional residue are dominated by broad diffraction peaks of cellulose (Fig. 3). However, mineral matter, mainly calcium sulfate and quartz, constituted the microwave liquefaction residue (Table 3). This indicates sufficient liquefaction of the lignocellulose components in the microwave-assisted method. The main components in the ashes of crop residue are silicon dioxide, potassium/sodium oxide, and calcium oxide according to reports (Jenkins et al., 1996; Capablo et al., 2009). Obviously, quartz in the residue is derived from the naturally present SiO₂ in corn stover. By reaction

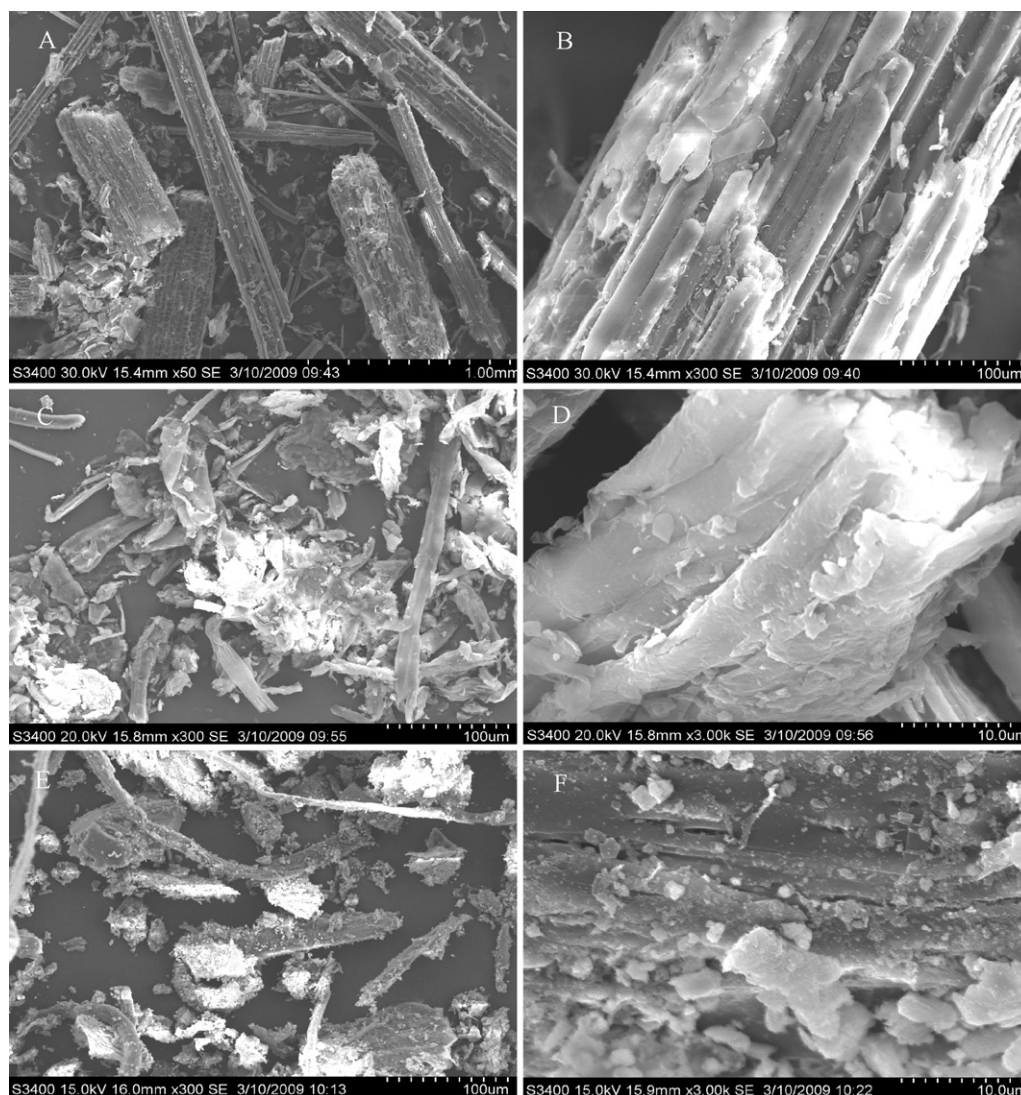


Fig. 4. SEM of raw corn stover and liquefaction residues. Note: A and B, raw corn stover 50 \times and 300 \times ; C and D, conventional liquefaction (120 min) residue 300 \times and 3000 \times ; E and F, microwave-assisted liquefaction (20 min) residue 300 \times and 3000 \times .

with H_2SO_4 at high liquefaction temperature, metal compounds form various sulphates including K_2SO_4 , Na_2SO_4 , and CaSO_4 . As calcium sulfate is less soluble than alkali metal sulphates, it remains in the residue to form the crystal.

In particular, the major diffraction planes of cellulose I, namely 101, $10\bar{1}$, and 002 are present at diffraction angles 2θ around 14.6, 16.6, and 22.7, respectively. Unlike a pure cellulose sample, the peaks of 101 and $10\bar{1}$ diffraction planes in the X-ray diffractograms of raw corn stover and liquefied corn stover residue overlapped and formed one broad peak (Fig. 3B and C). This is likely due to the existence of hemicellulose and lignin in the raw corn stover and

conventional residue. As more amorphous material was removed and a cellulose rich residue was then produced, CrI of cellulose increased from 49.6% to 69.3% after conventional liquefaction. Similar results have been also reported in previous investigations (Chang and Holtzapfle, 2000; Kasahara et al., 2001; Kim and Lee, 2005). The CrI of microwave-assisted liquefaction residue has not been determined for the weak diffraction of cellulose. The evident differences among the XRD patterns B, C, and D highlight that crystalline cellulose is the main resistance to conventional liquefaction while it more extensively dissolved in microwave-assisted liquefaction.

Table 3

Crystal components assignments for XRD.

Sample ^a	Main component	Corresponding peaks after fitting
A	Cellulose I	14.600, 16.588, 22.768, 34.850
B	Cellulose I	22.766, 34.547
C	Cellulose I	22.323, 34.512
	Gypsum	11.645, 20.741, 29.098
	Quartz	20.741, 26.579
D	Anhydrite	25.343, 31.278, 36.317, 38.577
	Quartz	20.866, 26.545

^a Sample name of A–D was the same as in Fig. 3.

3.5. Microstructure morphology of residues

The microstructure of the liquefaction residue by different methods was imaged by SEM (Fig. 4). As shown in Fig. 4A and B, very well organized and long compact fiber bundles are observed for the raw materials of corn stover. The residue size treated with conventional and microwave-assisted liquefaction is significantly smaller compared to the raw materials of corn stover at the same magnification of 300 times (Fig. 4C and E). It indicated that the rigid fiber bundles cracked into small irregular fragments during liquefaction. Many granules appeared on the surface of microwave

residue (Fig. 4E and F); while the conventional residue showed a relative glossy fiber-shaped texture (Fig. 4C and D). The small particles are probably the surface deposits of minerals residues after the liquefaction of lignocellulosic components (Capablo et al., 2009).

4. Conclusions

Significant differences in physicochemical and morphological properties were observed between conventional and microwave-assisted liquefaction products and residues. All the GPC and FTIR characteristics of the liquefied products indicate that microwave induced more intense oxidation cleavage of the lignocellulosic material and more extensive solvolysis reaction than conventional liquefaction. The XRD patterns indicate that crystalline cellulose is the main resistance to conventional liquefaction and it dissolved entirely in microwave-assisted liquefaction. Many granules on the surface of the microwave residue demonstrate the acceleration mechanism of microwave-assisted liquefaction. Microwave is a promising substitute for traditional heating method in biomass polyhydric alcohol liquefaction.

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