Rapid Liquefaction of Corn Stover with Microwave Heating

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Microwave heating was applied in the liquefaction of corn stover with polyhydric alcohol to establish a rapid process for converting corn stover into polyols. With ethylene glycol (EG) as liquefacient and 3.5% sulfuric acid as a catalyst, the residue content was reduced to 4.7% after 20 min of microwave liquefaction at 160 °C. Effects of liquefaction parameters on the residue content were investigated. It was found that the reaction temperature had a greater influence on the residue content than the sulfuric acid concentration and reaction time. The liquefied mixture was characterized as complexes of ester and ether type polyols by means of Fourier transform infrared spectroscopy. 3-(2-Methyl-1,3-dioxolan-2-yl) propanoic acid was characterized as the main degradation product of corn stover, besides the large amount of condensation product of EG.

Keywords: Liquefaction; Polyhydric alcohol; Corn stover; Microwave; FTIR; GC-MS

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INTRODUCTION

Because of the shortage of forest resources in China, crop residues are the greatest potential source of lignocellulosic raw materials. In 2013, China's output of crop residues was more than 729 million (Qiu *et al.* 2014). Research has revealed that lignocellulosic matter can be converted, in the presence of polyhydric alcohol, into multifunctional polyols, a promising source of chemicals (Yamada and Ono 1999; Lee *et al.* 2000; Kurimoto *et al.* 2000; 2001; Hassan and Shukry 2008). For example, liquefied corn bran (CB)-based polyol was obtained by the liquefaction of CB with a polyethylene glycol (PEG400)/glycerol mixed solvent. Subsequently, polyurethane foams were successfully prepared from the liquefied CB-based polyols (Lee *et al.* 2000).

Most conventional liquefaction utilizes external heating, such as oil bathing. The main drawback of this method is that the process takes about 1 to 3 h to attain a 70 to 90% liquefaction rate (Lee *et al.* 2000; Shin *et al.* 2009; Yan *et al.* 2010). A number of examples show that the use of microwave heating might improve the efficiency by dramatically shortening the reaction time (Valdemir *et al.* 2008; Xiao *et al.* 2008). Recently, microwave heating was successfully used for the liquefaction of wood with simple glycols (Kržan and Kunaver 2006; Kržan and Žagar 2009). The microwave liquefaction time was remarkably reduced to 10 to 20 min with organic acid anhydrides and phosphoric acid as a catalyst (Kržan and Kunaver 2006). However, to the best of the author's knowledge, no application of microwave heating for the polyhydric alcohol liquefaction of crop residue has been reported.

Corn stover (CS) is one of the most abundant agricultural residues in China, with a production of approximately 230 million tonnes annually (China Agriculture Yearbook

2007). Investigations on the polyhydric alcohol liquefaction of CS with microwave heating were carried out in the current study. The influence of various reaction conditions on the liquefaction of CS was analyzed, and the characteristics of liquefied product based mixture were also evaluated.

EXPERIMENTAL

Materials

The corn stover used in the experiments was dried and ground with a FW135 blade-mill (Tianjin City Taisite Instrument Co., Ltd., China) and then sieved through a 40-mesh screen. The reagents used were of chemical grade (Beijing Chemical Plant, China). The chemical composition of raw corn stover characterized to be 35.64% cellulose, 24.18% hemicelluloses, 8.73% acid-insoluble lignin, and 4.70% ash.

Methods

Microwave liquefaction

Liquefaction was carried out in a Milestone ETHOS Plus model system (Italy) equipped with 100 mL sealed Teflon reaction vessels with an internal temperature sensor. Samples were irradiated from 5 to 30 min under the selected starting microwave power, with sample temperature controlled to be between 130 to 180 °C. A typical reaction mixture consisted of 5.0 g CS powder, 25.0 g ethylene glycol (EG), and an appropriate amount of sulfuric acid (SA; 2.0 to 4.5 wt% *vs.* liquefaction reagent) as a catalyst. After liquefaction for a period of time (5 to 30 min), the vessels were allowed to cool to room temperature before opening.

Measurement of liquefaction extent and viscosity

After cooling, the liquefaction product was diluted with 80% 1,4-dioxane (Yao *et al*. 1994). The diluted resultant was filtered to separate the residue and filtrate. The residue was washed with 80% 1,4-dioxane (dioxane:water = 80:20 v:v), dried at 105 °C for 24 h in an oven, and then weighed. The residue content was defined as the percentage dry weight of the dioxane-insoluble substance to the total raw CS material (Eq. 1). This measure has traditionally been used as an index of the extent of liquefaction.

$$\text{Residue content (\%)} = \text{Residue weight (g)} / \text{Weight of raw material (g)} \times 100 \quad (1)$$

$$\text{Liquefaction yield (\%)} = 1 - \text{Residue content (\%)} \quad (2)$$

The viscosities of the liquefied products were measured using a NDJ-5S viscometer (Shanghai, China) at 25 °C.

Characterization of the liquefied product

Fourier transform infrared (FTIR) spectroscopy was used to study the change of CS components in the liquefaction reaction. The filtrate was condensed and freeze-dried for FTIR analysis on a Perkin Elmer 400 spectrometer (USA). Attenuated total reflection measurements were conducted for liquid samples and the solid sample was analyzed by the KBr pellet method.

Product identification was confirmed using an Agilent 7890A/5975C GC-MS System (USA). One gram of liquefied mixture was dissolved in 50 mL methanol for the GC-MS analysis. Chromatographic resolution was achieved with a 30 m × 250 µm DB-5 ms capillary column that had a 0.25 µm film thickness (J & W Scientific, Folsom, CA). The inlet temperature was set at 280 °C. The oven was maintained at an initial temperature of 50 °C for 3 min, then heated to 180 °C at the rate of 6 °C min^{-1}, and finally to 280 °C at 10 °C min^{-1} with a hold of 3 min. Helium gas was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The injection volume was 1.0 µL with a split ratio of 10:1. The ion source and quadrupole temperatures were 230 °C and 150 °C, respectively. Mass spectra were scanned from m/z 30 to 600 at a rate of 1.5 scans/s. The electron impact ionization energy was 70 eV. All the peak percentages were calculated by the method of area normalization.

Statistical analysis

All data collected was subject to analysis of variance ANOVA ($p<0.05$) using SPSS version 10.0 (USA).

RESULTS AND DISCUSSION

Effect of Liquefaction Reagents

The temperature produced during microwave irradiation significantly affects the liquefaction reaction kinetics. Dielectric properties of the solvent utilized in microwave heating play an important role in microwave heating. Materials with different dielectric properties will have a different response to microwave radiation (Kormin *et al*. 2013). Normally, the dielectric properties of material consists of two major parts: dielectric constant representing the ability of materials to obstruct or store the electromagnetic energy as it passes through and the dielectric loss representing the ability of materials to convert that stored energy to heat (Souleyman *et al*. 2014). Both dielectric constant and dielectric loss are functions of frequency, temperature, and types of materials (Robinson *et al.* 2012). Therefore, it is hard to predict the heating curves by only one parameter. We examined the heating characteristics of three widely used polyhydric alcohol liquefactants: EG, glycerin, and PEG400/glycerin (4:1). The temperatures of the three liquefaction systems reached about 180 °C in 2 min with microwave irradiation at 600 W. The temperature increase rates of the three systems under microwave irradiation were very close, as shown in Fig. 1. This indicates that each of the three types of liquefaction solvents absorbs microwave energy efficiently and can be heated up to a fixed temperature in a short time.

To seek a suitable polyhydric solvent for the reaction, liquefaction results of the three liquefaction systems were compared. The reaction mixture (5.0 g CS mixed with 25.0 g liquefaction reagent and 0.875 g sulfuric acid) was heated to 150 °C with the irradiation power of 600 W. It was maintained at the predetermined temperature (150 °C) for 20 min by automatic microwave irradiation. The percentage of residue contents liquefied with EG and PEG400/glycerin (4:1) were 7.53% and 7.58%, respectively, while the residue with glycerin was as high as 27.11%. As EG was efficient and inexpensive, it was chosen as the liquefying reagent in this study.

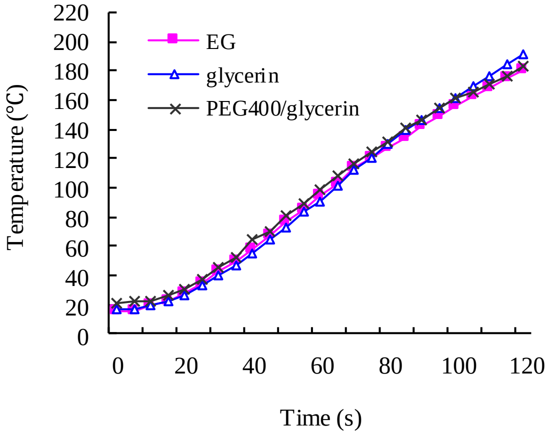

Fig. 1. Temperature curve of three liquefaction reagents. Microwave power 600 W; liquefying reagent EG, glycerin, PEG400/glycerin (4:1), 50 g

Effect of Microwave Power

The microwave system used in this study was controlled by temperature feedback. This means that the microwave irradiated at the selected power until the temperature reached the predetermined value, and then the power was varied according to feedback to keep the preset temperature. To investigate the effect of microwave power on the liquefaction process, 5.0 g CS mixed with 25.0 g EG and 0.875 g SA was heated to 150 °C. The irradiation power was varied from 400 to 1000 W, but the temperature was kept constant for 20 min. The residue content decreased significantly from 15.57% to 7.36% when the microwave power changed from 200 W to 400 W, as shown in Fig. 2. No significant decrease in residue content (p>0.05) was observed when microwave power was further increased from 400 W to 1000 W. The viscosity continually decreased when microwave power increased from 200 to 600 W. A low viscosity of 202 mPa.s was achieved at 600 W and provided better fluidity for the liquefied product of CS. Therefore, the starting microwave power was set to 600 W in the subsequent experiment.

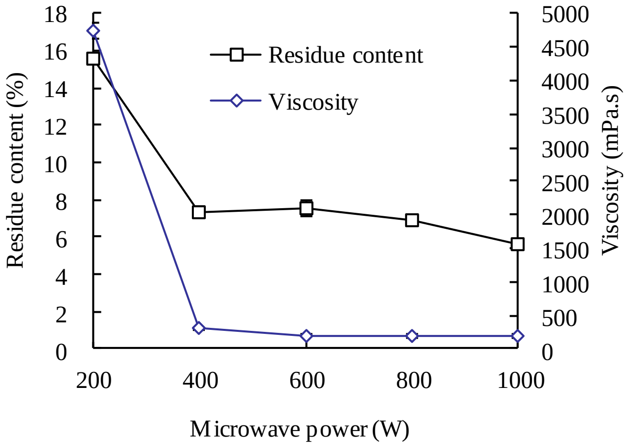

Fig. 2. Effect of microwave power on residue content and viscosity of CS liquefied product. Liquefying reagent, EG; SA, 3.5%; temperature, 150 °C; time, 20 min

Effect of Sulfuric Acid Concentration

Sulfuric acid (SA) was used in the liquefaction due to its reportedly strong catalytic effect to polyhydric solvolysis (Kurimoto *et al.* 2001; Hassan and Shukry 2008). The effect of the ratio of SA to liquefaction reagent (m/m; %) was investigated in Fig. 3. Residue content decreased while SA concentration increased from 2.0 to 3.5 wt% and reached a minimum at 6.91% with 3.5% SA. The residue content increased as SA concentration increased further. This was ascribed to high SA concentration (>3.5%) accelerating the repolymerization of liquefied small molecules into insoluble residue (Yao *et al.* 1993, 1994). Excessive catalyst caused a significant ($p<0.05$) increase in viscosity in Fig. 3 for the same reason. These results indicate that 3.5% SA is sufficient for the microwave-assisted liquefaction.

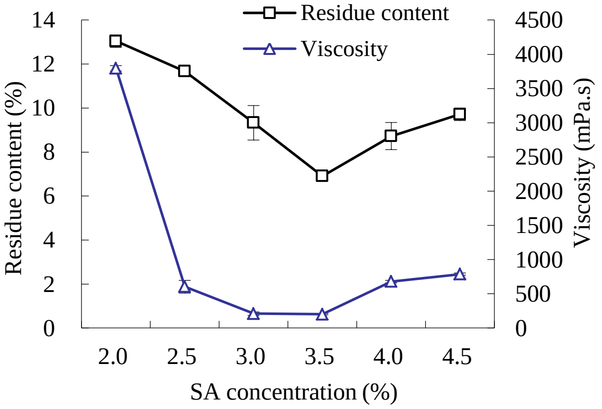

Fig. 3. Effect of sulfuric acid concentration on residue content and viscosity of CS liquefied product. Microwave power 600 W; liquefying reagent, EG; temperature, 150 °C; time, 20 min

Effect of Reaction Temperature

Figure 4 shows the effect of reaction temperature on the residue content of CS. The residue content of CS noticeably decreased as the liquefaction temperature increased from 130 °C to 160 °C. Further increase in the liquefaction temperature from 160 °C to 180 °C resulted in a slight decrease in the amount of residue with black insoluble residue observed.

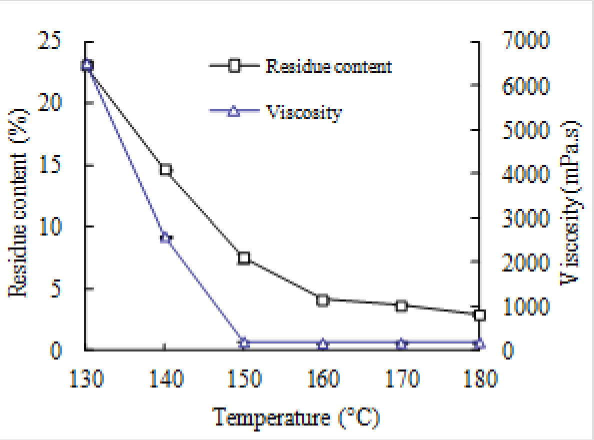

Fig. 4. Effect of reaction temperature on residue content and viscosity of CS liquefied product. Microwave power 600 W; liquefying reagent, EG; SA, 3.5%; time, 20 min

The appearance of black insoluble residue indicated recondensation reactions at high liquefaction temperatures, as reported by Yamada (1999) and Rezzoug and Capart (2002). A similar trend was observed for viscosity in Fig. 4. Accordingly, it could be concluded that 160 °C is the suitable liquefaction temperature for the liquefaction system.

Effect of Liquefaction Time

The residue content and viscosity as a function of liquefaction time is shown in Fig. 5. The viscosity decreased significantly ($p<0.05$) when reaction time was extended from 5 min to 15 min. No decrease was observed after 15 min. The changes in the residue content corresponded to the reaction balance between degradation and repolymerization in the liquefaction progress. During the first 20 min of the liquefaction, the degradation dominated the process, which resulted in residue content declining rapidly to approximately 4.1%. Beyond that time, the percentage of residue increased slightly, and black insoluble matter was observed in the residue as a consequence of liquefied fragments repolymerizing into insoluble macromolecules. The reaction time was reduced significantly from several hours to 20 min as compared to conventional liquefaction as shown in Table 1.

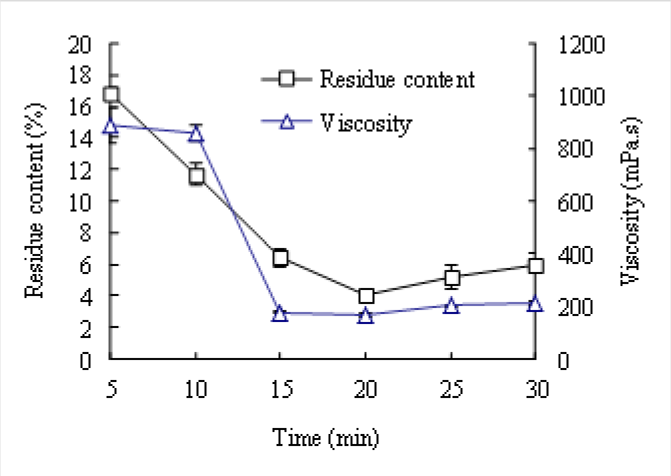

Fig. 5. Effect of liquefaction time on residue content and viscosity of CS liquefied product. Microwave power 600 W; SA, 3.5%; temperature, 160 °C; liquefying reagent, EG.

Table 1. Liquefaction Parameters Compared with Literature

Feedstock	Time	Temperature	Liquefaction reagent	Sulfuric acid concentration	Solvent ratio	Yield	Reference
corn stover	2 h	170°C	EG:EC=9:1	3%	3:1	91%	Yu *et al.* 2006
cornstalk	3 h	170°C	PEG400:glycerine=4:1	3%	10:3	90%	Yan *et al.*, 2010
newspaper	60 min	160°C	EG:EC = 8:2	3%	3:1	70%	Shin *et al.*, 2009
corn stover	20 min	160°C	EG	3.5%	5:1	95%	

Note: EC is the abbreviation of ethylene carbonate

Characterization of Liquefied Products with FTIR

The spectra of the three samples in Fig. 6 were different except for the strong absorptions from 3400 to 3300 cm^{-1}. The bands at 3409 cm^{-1}, 2903 cm^{-1}, 1426 cm^{-1}, 1374 cm^{-1}, 1162 cm^{-1}, and 1054 cm^{-1} in the spectra of CS samples in Fig. 6a validated the presence of cellulose. Similarly, the bands between 1800 to 900 cm^{-1} in Fig. 6a were recognized as the fingerprint region for lignin (Smidt *et al.* 2008), and the absorption of the C=O group at 1735 cm^{-1} in Fig. 6a was attributed to the hemicellulose contained in CS (Yang *et al.* 2007). In the spectra of EG in Fig. 6b, the absorption at 1034 cm^{-1} and 1083 cm^{-1} was due to C-O stretching and C-O deformation. The bands at 3386 cm^{-1} (O-H), 2877 cm^{-1} (C-H), and 1060 cm^{-1} (C-O) in Fig. 6c indicated the existence of polyols, which resulted from the degradation of cellulose in the liquefied product of CS. Compared with the spectra of CS and EG, the emergence of a sharp C=O stretching peak at 1731 cm^{-1} and the C-O stretch at 1207 cm^{-1} in the spectrum of liquefied product of CS in Fig. 6c was attributed to the formation of ester. The strong absorption at 1125 cm^{-1} (C-O-C) indicated the presence of ether in the liquefied product (Yang *et al.* 2009). Therefore, it can be concluded that the liquefied mixture contained mainly ester/ether type polyols formed by the degradation, oxidation, and recondensation of the CS components and EG.

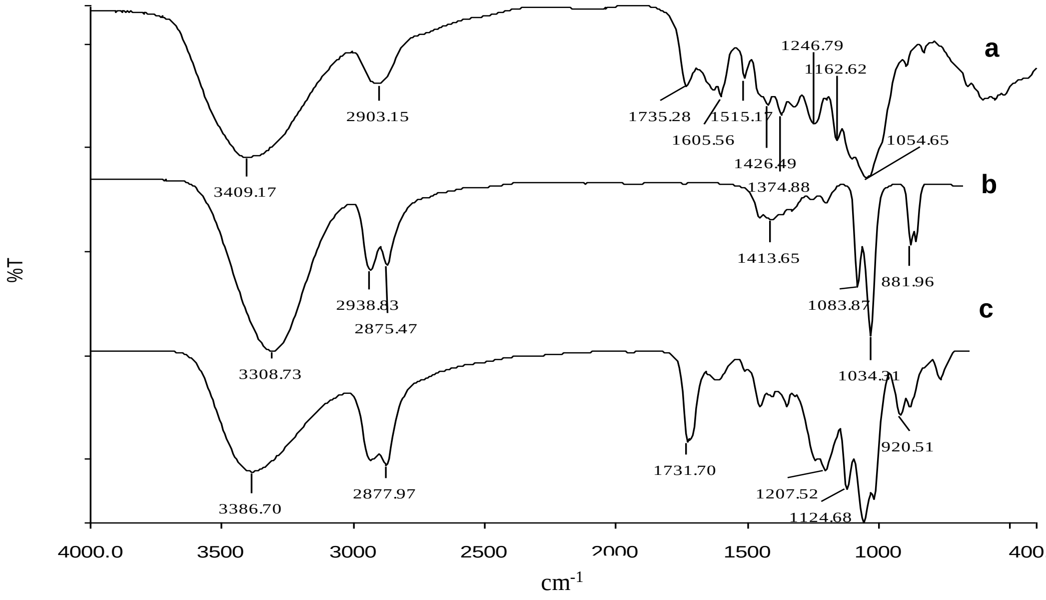

Fig. 6. FTIR spectra of (a) CS, (b) EG, and (c) liquefied product of CS after 20 min

Characterization of Liquefied Products with GC-MS

Gas chromatography-mass spectrometry (GC-MS) was used to identify the chemical composition of microwave liquefied CS. The chromatogram is shown in Fig. 7. The major compounds detected by GC-MS are listed in Table 2. The area % may be used to show relative concentration of the compound in the sample. As shown in Fig. 7 and Table 1, the major compounds in microwave liquefied CS are categorized as two types: one is EG and its derivatives, including DEG and TEG, and the other are methyl esters, including 3-(2-methyl-1, 3-doxolane-2-yl) propionic acid methyl ester, levulinic acid isopropyl ester, methyl laurate, and methyl hexadecanoate. The EG derivatives dominated the liquefied product, as has been reported (Zhan *et al.* 2003; Zhang *et al.*

2007). Compounds in the latter category were assumed to be degraded from lignocellulosic components, among which PAME was dominant. 3-(2-Methyl-1,3-dioxolan-2-yl) propanoic acid methyl ester was detected in the thermal solvolysis products of cellulose (Vidal *et al.* 1992). Zhang *et al.* (2012) reported 3-(2-methyl-1,3-dioxolan-2-yl) propanoic acid ethyl ester in the liquefied compounds from acid hydrolysis residue of corncob in EG. The GC-MS results were in accordance with those from FTIR. The qualitative analysis will greatly facilitate the high-value utilization for the liquefaction products.

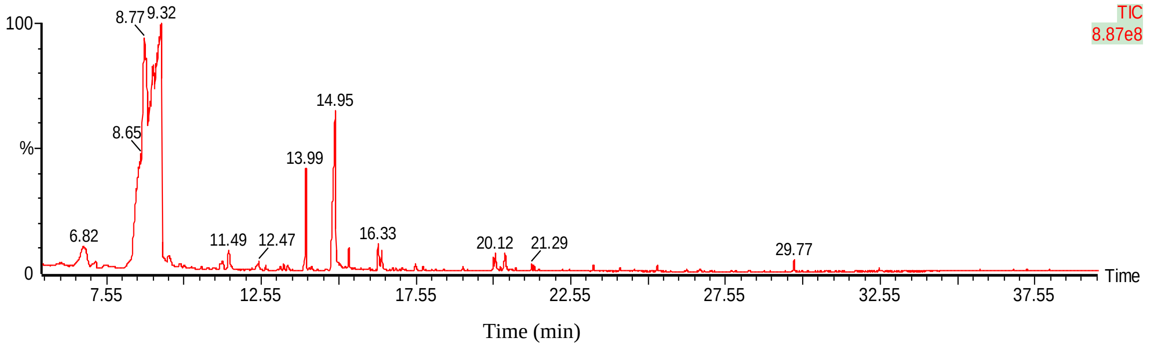

Fig. 7. GC-MS chromatograph of liquefied product of CS after 20 min

Table 2. Major Compounds in Liquefied Product of CS at 20 Min

RT (min)	Component	Formula	Relative area (%)
9.32	Ethanol,2,2'-oxybis	$C_4H_{10}O_3$	63.66
11.49	2-Isopropoxyethyl proponate	$C_8H_{16}O_3$	1.76
13.99	3-(2-methyl-1,3-doxolane-2-yl) propionic acid methyl ester	$C_8H_{14}O_4$	4.65
14.95	Triethylene glycol	$C_6H_{14}O_4$	19.05
16.33	Levulinic acid isopropyl ester	$C_8H_{14}O_3$	1.32
20.12	1,6-dioxaspiro[4,4]nonane-2,7-dione	$C_7H_8O_4$	0.81
21.29	Methyl laurate	$C_{13}H_{26}O_2$	0.29
29.77	Methyl hexadecanoate	$C_{17}H_{34}O_2$	0.51

CONCLUSIONS

1. Rapid polyhydric alcohol liquefaction of CS was achieved by using microwaves as a heating source. With EG as the polyhydric alcohol solvent and sulfuric acid as a catalyst, it only took 20 min to obtain a low residue content of 4.7%.
2. Microwave heating dramatically promoted the acid-catalyzed solvolysis of lignocellulose and gave several times faster liquefaction rates than conventional external heating methods.
3. The effects of processing parameters, including temperature, acid concentration, microwave power, and reaction time on the residue content, were revealed to be

significant. The reaction temperature has a greater influence on the residue content than the sulfuric acid concentration and reaction time.

4. The liquefied product was characterized as a mixture of ester and ether, according to the FTIR spectra. The GC-MS further identified EG derivatives and methyl esters as the major components in the liquefied products.

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