Influence of Microwave Heating on the Liquefaction Kinetics of Corn Stover in Ethylene Glycol

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The microwave liquefaction kinetics of corn stover in the presence of ethylene glycol (EG) using sulfuric acid as a catalyst was studied. The liquefaction apparent rate constant (*k*) was examined using a first-order reaction model. The *k* values of corn stover increased from 0.080 min^{-1} to 0.165 min^{-1}, with the reaction temperature increasing from 120 ^{o}C to 180 ^{o}C. The *k* value of cellulose at 160 ^{o}C was close to that of corn stover, indicating that cellulose was involved in the rate-determining step in the microwave liquefaction. The microwave liquefaction rate of corn stover at 160 ^{o}C was seven times greater than that of conventional liquefaction with external heating. The apparent activation energy (E_a) was 22.6 kJ mol^{-1} and the frequency factor (*A*) was found to be 12.98×10^{5} s^{-1}. The decrease in apparent activation energy and the increase in the frequency factor as compared to conventional liquefaction kinetic parameters indicates a non-thermal effect of microwave in the liquefaction of corn stover, which explains the acceleration mechanism of liquefaction with microwaves.

Keywords: Microwave; Liquefaction; Corn stover; Kinetics

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INTRODUCTION

The shortage of fossil fuel resources in China has attracted increasing attention to the utilization of lignocellulosic resources in recent years. The polyhydric liquefaction of biomass was a promising way to turn the solid biomass into a chemical feedstock for polyurethane (Yamada and Ono 1999; Kurimoto *et al.* 2000; Lee *et al.* 2002; Chen and Lu 2009). Disadvantages of conventional liquefaction with external heating are the low efficiency and low yield. Microwave heating is becoming a widely accepted tool for chemists.

Numerous studies have revealed advantages from microwave-assisted synthesis, including reaction acceleration, yield improvement, enhanced physicochemical properties, and the evolution of new material phases (Shi *et al.* 2003). Microwave-assisted liquefaction has also been utilized in the field of lignocellulosic biomass recently (Kržan and Kunaver 2006; Pan *et al.* 2011; Xu *et al.* 2012). The application of microwave technology to the polyhydric liquefaction of biomass offers several advantages over conventional heating liquefaction, including saving processing time and improving the liquefaction yield as reported by our previous work (Xiao *et al.* 2011).

There has been considerable speculation and discussion of the acceleration effect. Much of the debate has centered on the thermal microwave effects arising from the rapid heating and high bulk reaction temperatures attained with microwave dielectric heating, or whether some effects are connected to so-called specific or nonthermal microwave effects (Kappe *et al.* 2013). To explain the acceleration mechanism of microwave on the liquefaction reactions of corn stover, the reaction kinetics were studied.

EXPERIMENTAL

Materials and Chemicals

Corn stover used in the experiments was dried and ground with a blade-mill (FW135 medicine mill, China), followed by sieving through a 40-mesh screen. The reagents were of chemical grade (Beijing Chemical Plant, China).

Corn stover was analyzed for cellulose, hemicelluloses, lignin, and acid-insoluble ash according to the method by Van Soest *et al.* (1991). The chemical compositions of corn stover are listed in Table 1.

Table 1. Chemical Compositions of Corn Stover

Components	Cellulose	Hemicelluloses	Lignin	Acid-insoluble ash
Content (%)	37.34±0.38	30.51±0.72	8.73±0.15	0.91±0.10

In this study cellulose powder, xylan, and lignin alkali (C6288, X4252, 471003 from Sigma Aldrich) were used as model compounds of liquefaction kinetics. Cellulose was in white powder form, and lignin was alkali lignin in black powder form. Xylan, in yellow powder form, was used as a representative component of hemicelluloses in liquefaction processes.

Liquefaction Procedure

Liquefactions were carried out in a Milestone microwave labstation (Ethos Touch Control, Italy, maximum output 1000 W, ASM-400 magnetic stirrer) equipped with 100 mL sealed teflon reaction vessels and an internal temperature sensor (ATC-400-CE automatic temperature control up to 300 ^oC with fiber optic sensor). The frequency used by the microwave system was 2450 MHz. The system featured both single-mode and multi-mode technologies in a single labstation. The samples were irradiated for less than 2 min under 600 W as the starting microwave power. The sample temperature was controlled at 160 ^oC for the preset duration from 1 to 25 min with the microwave power changed. The reaction mixture consisted of 5.0 g of corn stover, 25.0 g of the liquefaction reagent ethylene glycol (EG), and 0.875 g of the catalyst sulfuric acid. After liquefaction for a preset time, the vessels were allowed to cool at room temperature before they were opened.

After cooling, the liquefaction product was diluted with 80% of 1,4-dioxane (1,4-dioxane:water = 80:20, v:v). The diluted resultant was filtered and the residue was dried at 105 ^oC for 12 h in an oven and then weighed. All of the experiments were done in triplicate.

The liquefaction yield was calculated by the following equation:

$$\text{Liquefaction yield (\%)} = (1\text{- weight of residue/weight of crop material}) \times 100\% \quad (1)$$

Modeling Methods

As the initial concentration of the liquefying reagent, EG, is much larger than the concentration of the crop residues, the concentration of EG will not change appreciably during the course of the reaction. The concentration of the reactant in excess will remain almost constant. The rate's dependence on crop residues can be isolated, and the rate law can be written as a pseudo-first-order reaction model (Yamada and Ono 1999; Liang *et al.* 2006; Yu *et al.* 2006),

$$R = A\exp(-kt) \tag{2}$$

where k is the apparent rate constant, A is the constant of integration, and R is the mass of the unliquefied component which is equal to the extent of the residue content.

Equation (2) can also be written as:

$$\ln R = \ln A - kt \tag{3}$$

The value of R at different times could be obtained from the experimental data. Plotting the ln$R$ against time created a straight line with a slope of $-k$. The apparent rate constant, k, was used to evaluate the liquefaction reaction rate under different conditions in our study.

Statistical analysis

All of the data collected were subjected to analysis of variance ANOVA ($P < 0.05$) using SPSS. Kinetics data was subject to the analysis of linear regression using Excel.

RESULTS AND DISCUSSION

Microwave Liquefaction Yield of Model Compounds

The time-dependence of the liquefaction curves of cellulose, hemicelluloses, and lignin at 160 °C are shown in Fig. 1.

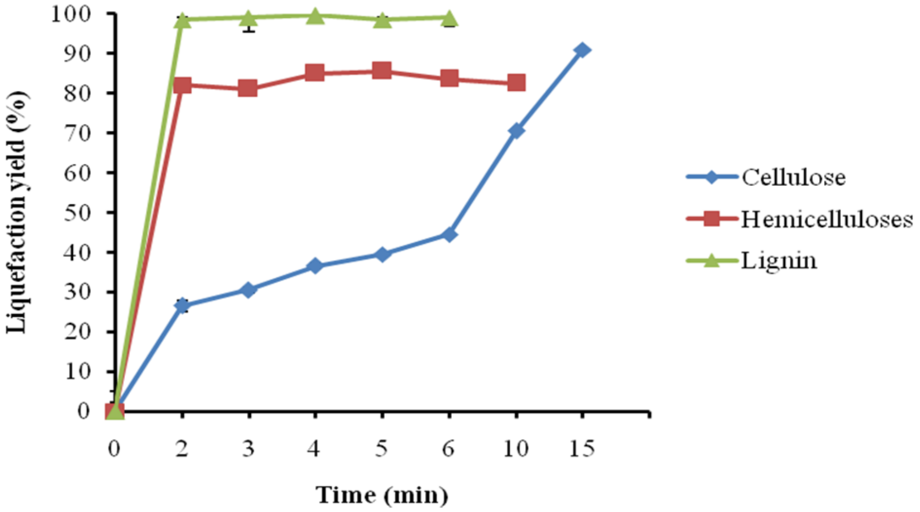

Fig. 1. Microwave liquefaction yield of model compounds at 160 °C

It could be seen that, with the increase of reaction time, the liquefaction yield of cellulose increased significantly. The liquefaction yield increased to 91.0% after liquefaction for 15 min. The liquefaction yield of hemicelluloses and lignin were up to 82.0% and 98.5%, respectively, in 2 min, and they remained at the same level with the progress of time. The results showed that hemicelluloses and lignin reacted much more easily in the microwave liquefaction than cellulose did.

Microwave Liquefaction Yield of Corn Stover under Different Temperature

The time-dependences of the liquefaction curves for corn stover at 120 °C, 140 °C, 160 °C, and 180 °C are shown in Fig. 2. It can be seen that, with the increase of reaction time, the liquefaction yield of corn stover increased significantly in the early stage. It decreased obviously when the microwave liquefaction time was beyond 15 min at 120 °C and at 180 °C. There are mainly two reactions in the entire lignocellulosic liquefaction, *i.e.,* decomposition and polycondensation (Niu *et al.* 2011). It is reasonable that polycondensation among the degraded product might be accelerated at a high temperature of 180 °C, while the obvious increase of residue at 120 °C at the late stage was supposed to be the result of areaction among degraded products and abundant undegraded residue. Polymerization was also observed under 140 °C liquefied for 25 min. To describe the liquefaction kinetics, the time investigated in our modeling was limited to the duration without obvious condensation.

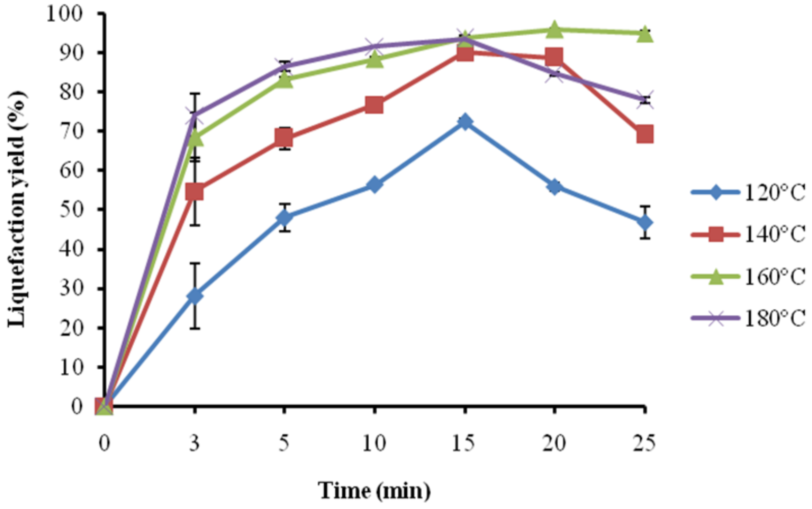

Fig. 2. Microwave liquefaction yield of corn stover at different temperatures

Microwave Liquefaction Kinetic Modeling

With the data in Fig. 2, it was decided to choose the duration without obvious polycondensation to fit with a first order reaction according to Eq. (3). Plotting the ln$R$ of corn stover against time gave rise to Fig. 3. The linear fitting results are shown in Table 2. It can be seen that the microwave liquefaction apparent rate constant k of corn stover increased with increasing temperatures, which indicated that microwave liquefaction could be accelerated by an increase in temperature. The apparent rate constant of corn stover increased by two times when the liquefaction temperature was increased from 120 °C to 180 °C.

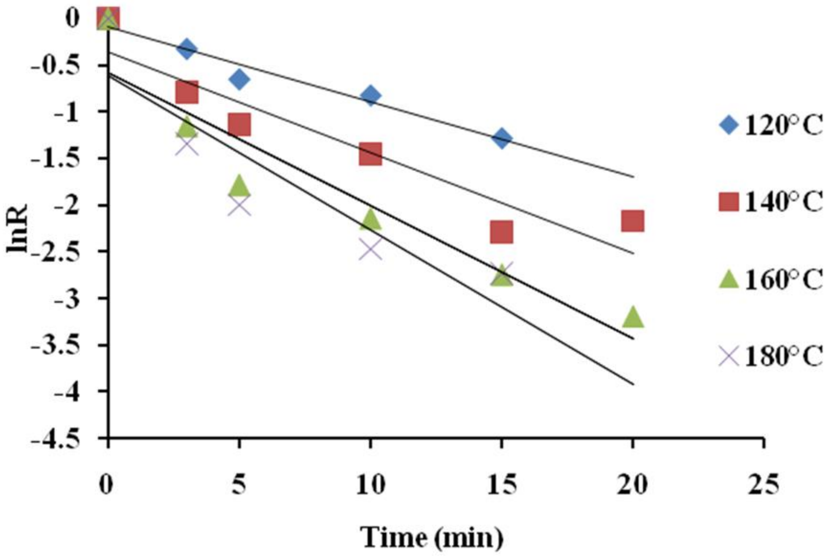

Fig. 3. Relation between microwave liquefaction reaction rates and reaction times

Table 2. Fitting Results of Microwave Liquefaction of Corn Stover

Temperature (^oC)	Linear equation	R^2	Apparent rate constant *k* (/min)
120	y=-0.080x-0.087	0.959	0.080
140	y=-0.107x-0.362	0.889	0.107
160	y=-0.142x-0.575	0.897	0.142
180	y=-0.165x-0.619	0.808	0.165

Similarly, with the data in Fig. 1, plotting of the ln*R* of cellulose against time resulted in a linear fitting equation, which was y=-0.157x+0.156 (R^2=0.950). The apparent rate constant of 0.157/min was close to that of corn stover at 160 °C. This demonstrated that cellulose was the rate determining step in the microwave liquefaction of corn stover, since hemicelluloses and lignin were degraded quickly at the initial period of liquefaction.

Analysis of Microwave Liquefaction Kinetic Parameter

The solvolysis liquefaction kinetics for biomass have been studied by many researchers (Yamada and Ono 1999; Liang *et al.* 2006; Yu *et al.* 2006; Yan *et al.* 2010; Shin *et al.* 2009). The liquefaction rate constant *k* of corn stover at 160 ^oC is 0.0191 min^{-1} in EG (Liang *et al.* 2006) and 1.27 h^{-1} in EG:EC (9:1) (Yu *et al.* 2006). It could be concluded that the apparent rate constant of microwave liquefaction was seven times greater than that of the conventional method.

According to the Arrhenius equation, the relation between the reaction apparent rate constants and the reaction temperatures can be expressed as follows,

$$\ln k = \ln A - E_a/RT \tag{4}$$

where E_a is the apparent activation energy, *R* is the ideal gas law constant (8.314 J/mol.K), and *A* is the pre-exponential factor.

For the liquefaction of corn stover in EG, the relationship between the ln*k* and 1/*T* in Table 1 is plotted in Fig. 4. After linear fitting, the apparent activation energy value (E_a) and the pre-exponential factor (*A*) were calculated from the regression equation in Fig. 3. As shown in Table 3, in contrast to conventional liquefaction, the apparent activation energy for corn stover under microwave liquefaction was E_a=22.6 kJ/mol, which is 3.3 times lower than the E_a under conventional liquefaction (Yan *et al.* 2010), while the value of the pre-exponential factor for the microwave condition is 1.5 times higher than the value of the conventional method.

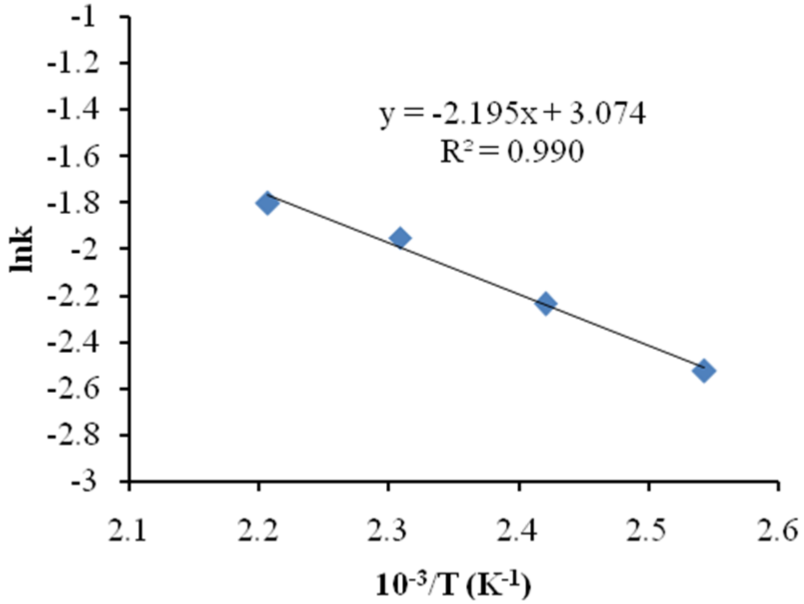

Fig. 4. Arrhenius plot of the microwave liquefaction of corn stover in EG

Table 3. Comparison of Kinetic Parameters between Conventional and Microwave Liquefaction

Method	Apparent activation energy E_a	Pre-exponential factor *A*
Conventional	73.6 kJ/mol [a]	8.8×10^5/s [a]
Microwave	22.6 kJ/mol	12.98×10^5/s

Note[a] indicates data from literature (Yan *et al.* 2010)

The comparison of kinetic results between conventional heating experiments and microwave-assisted liquefaction indicated the presence of a non-thermal microwave effect, which was classified as the acceleration of chemical processes in a microwave field that could not be rationalized in terms of either purely thermal/kinetic or specific thermal microwave effects. According to Perreux and Loupy (2001), specific microwave effects can also be expected for the polar mechanism, in which the polarity is increased during the reaction from the ground state toward the transition state. The outcome is essentially dependent on the solvent medium and the reaction mechanism. Yamada and Ono (2001) reported that when using EG as a solvolysis reagent, cellulose was degraded and produced a considerable amount of EG glucosides at the early stage of the reaction, which could be regarded as the transition state. The liquefaction was initiated by a nucleophilic reaction between EG and the lignocellulosic feedstock. The apparent activation energy (E_a) may be regarded as the minimum energy required to start the liquefaction of corn stover. The greater polarity of the solvent medium, EG, and the lignocellulosic substance will facilitate the nucleophilic attack. Therefore, the energy required for the ground state toward the transition state, *i.e*. apparent activation energy, was reduced.

The pre-exponential factor, *A*, is representative of the probability of a molecular impact. The collision efficiency can be effectively influenced by the orientation of the polar molecules involved in the reaction under microwave irradiation (Perreux *et al.* 2001). Binner *et al.* (1995) also reported the role of the pre-exponential factor in explaining increased reaction rates observed during the microwave synthesis of titanium carbide.

CONCLUSIONS

1. Liquefaction of cellulose was found to be the rate-determining step among the three major components in lignocellulosic material.
2. The microwave liquefaction kinetics of corn stover fitted a first-order reaction model well.
3. The *k* values increased by a factor of two with the reaction temperature increasing from 120 ^{o}C to 180 ^{o}C. The microwave liquefaction rate at 160 ^{o}C was seven times faster than that of the conventional liquefaction.
4. The apparent activation energy (E_a) decreased to 22.6 kJ mol^{-1}, and the frequency factor (*A*) increased to 12.98×10^{5}s^{-1} as compared to the conventional liquefaction parameters, 73.6 kJ mol^{-1} and 8.8×10^{5} s^{-1}, respectively.
5. The changes in the apparent activation energy and frequency factor were interpreted, theoretically, based on the non-thermal effect of microwave in the liquefaction of corn stover.

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REFERENCES CITED

Binner, G., Hassine, A., and Cross, T. (1995). “The possible role of the pre-exponential factor in explaining the increased reaction rates observed during the microwave synthesis of titanium carbide,” *J. Mater. Sci.* 30, 5389-5393.

Chen, F., and Lu, Z. (2009). “Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products,” *J. Appl. Polym. Sci.* 111(1), 508-516.

Kappe, O., Pieber, B., and Dallinger, D. (2013). "Microwave effects in organic synthesis: Myth or reality?" *Angew. Chem.* 52(4), 1088-1094.

Kržan, A., and Kunaver, M. (2006). "Microwave heating in wood liquefaction," *J. Appl. Polym. Sci.* 101(2), 1051-1056.

Kurimoto, Y., Takeda, M., Koizumi, A., Yamauchi, S., Doi, S., and Tamura, Y. (2000). "Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI," *Bioresour. Technol.*74(2), 151-157.

Lee, S.H., Teramoto, Y., and Shiraishi, N. (2002). "Biodegradable polyurethane foam from liquefied waste paper and its thermal stability, biodegradability, and genotoxicity," *J. Appl. Polym. Sci.* 83(7), 1482-1489.

Liang, L., Mao, Z., Li, Y., Wan, C., Wang, T., Zhang, L., and Zang, L. (2006). "Liquefaction of crop residues for polyol production," *BioResources* 1(2), 248-256.

Niu, M., Zhao, G., and Mehmet, H. A. (2011). "Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: A review," *For. Stud. China* 13(1), 71-79

Pan, H., Zheng, Z. F., and Hse, C. Y. (2011)."Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams," *Eur. J. Wood Wood Prod*. 69(3), 1-10.

Perreux, L., and Loupy, A. (2001). "A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations," *Tetrahedron* 57, 9199-9223.

Shin, H., Kim, C., and Kim S. (2009)."Kinetic study of recycled newspaper liquefaction in polyol solvent," *Biotechnol. Bioprocess Eng.*14(3), 257-382.

Van Soest, P., Robertson, J., and Lewis, B. (1991). "Methods for dairy fiber, neutral detergent fiber and nonstarch polysaccharides in relation to animal nutrition," *J. Dairy Sci.* 74, 3583-3597.

Xiao, W. H., Han, L. J., and Zhao, Y. Y. (2011). "Comparative study of conventional and microwave-assisted liquefaction of corn stover in ethylene glycol," *Ind. Crop. Prod.* 34(3), 1602-1606.

Xu, J. M., Jiang, J. C., Hse, C. Y., and Shupe, T. F. (2012). "Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy," *Green Chem.*14, 2821-2830.

Yamada, T, and Ono H. (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose," *J. Wood Sci.* 47(6), 458-464.

Yamada, T., and Ono, H. (1999)."Rapid liquefaction of lignocellulosic waste by using ethylene carbonate," *Bioresour. Technol.* 70(1), 61-67.

Yan, Y. B., Hu, M. M., and Wang, Z. H. (2010). "Kinetic study on the liquefaction of cornstalk in polyhydric alcohols,"*Ind. Crop. Prod.*32(3), 349-352.

Yu, F., Ruan, R., Lin, X., Liu, Y., Fu, R., Li, Y., Chen, P., and Gao, Y. (2006). "Reaction kinetics of stover liquefaction in recycled stoverpolyol," *Appl. Biochem. Biotechnol.* 129-132, 563-573.

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