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Kinetic study on the liquefaction of cornstalk in polyhydric alcohols

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ABSTRACT

The powders of cornstalk were liquefied in polyhydric alcohols using sulfuric acid as catalyst at 130–190 °C for different reaction times. The kinetics along with liquefaction ratio was analyzed using kinetic models under different reaction temperatures. The result indicated that the liquefaction of cornstalk in polyhydric alcohols was multilevel. The apparent reaction rate constants increased with the increase of reaction temperatures. The apparent activation energy (E') was 73.6 kJ mol^{-1} and the apparent frequency factor (A') was found to be 8.8×10^5 S^{-1}. According to transition-state theory, the apparent activation free enthalpy ($\Delta G'$), apparent activation enthalpy ($\Delta H'$), and apparent activation entropy ($\Delta S'$) of liquefaction reaction slightly changed with temperature. With regards to apparent activation enthalpy, the result indicated that the liquefaction of cornstalk in polyhydric alcohols was predominantly an endothermic reaction in nature.

1. Introduction

The conversion and effective utilization of lignocellulosic biomass, which is abundant and reproducible, is increasingly received interest due to the perceived need for the reduction of consumption of fossil energy and environmental protection. Especially for China, which is an agricultural country, there are nearly 7×10^8 ton crop byproducts, such as sugarcane bagasse, cornstalk, wheat straw, and wood wastes, which are abundantly reproducible resource in nature (Sun and Sun, 2006). Thus, it is significant for energy strategy to use these crop byproducts efficiently for our country. However, lignocellulosic biomass is composed mainly of cellulose, hemicellulose and lignin, which are of thermosetting polymer, and therefore cannot be processed easily like thermoplastic polymer, glasses and metal. In the past decades, many attempts and efforts have been made to utilize lignocellulosic biomass much more efficiently by applying chemical and biochemical techniques, such as pyrolysis (Sharma and Rao, 1999), modification (Nakano, 1994), hydrolysis (Chio and Mathews, 1996) and liquefaction (Kurimoto et al., 1999; Pu and Shiraishi, 1993; Yamada and Ono, 1999; Yao et al., 1993, 1994). Especially for liquefaction in solvents, biomass could be decomposed into liquid at mild temperature and atmospheric pressure, which could be used as fuel and chemical raw materials.

There were two kinds of liquefaction solvents in common use, which were polyhydric alcohols (Kurimoto et al., 1999; Yamada and Ono, 1999; Yao et al., 1993) and phenol (Pu and Shiraishi, 1993). Accordingly, the liquefaction reactions involving the two kinds of solvents were called alcoholysis and phenolysis, respectively. The liquefied products could be used to prepare polyurethane, phenolic resin (Lin et al., 1995) and corresponding materials, such as foam (Yao et al., 1995), film (Kurimoto et al., 2000, 2001) and adhesive (Alma and Basturk, 2006). In order to use liquefied products more effectively, it was of great importance to identify liquefied products and analyze reaction mechanisms. Because of the complexity of the components of biomass, it was mainly focused on using cellulose and lignin models to analyze the liquefaction reaction pathways (Lin et al., 1997a,b,c, 2001a,b; Yamada et al., 1996; Yamada and Ono, 1999, 2001; Zhang et al., 2006).

Renewed interest in the utilization of lignocellulosic biomass as sources of energy and chemicals has necessitated an understanding of the liquefaction reaction kinetics, which is helpful in investigating the effect of experimental variables on liquefaction reaction rate. Alma and co-workers had studied the kinetics of wood phenolysis, using hydrochloric acid and sulfuric acid as catalysts (Acemioglu and Alma, 2002; Alma and Acemioglu, 2004). And also the kinetics of pyrolysis and hydrolysis had been investigated (Chio and Mathews, 1996; Sharma and Rao, 1999). However, there was no kinetic study on the liquefaction of lignocellulosic biomass in polyhydric alcohols. In the past, we had prepared biomass-based polyurethane foams successively, using the liquefied products of cornstalk and sugarcane bagasse in polyhydric alcohols (Yan et al., 2008, 2009). In this paper, the liquefaction reaction kinetics

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in polyhydric alcohols was studied, using cornstalk as raw material.

2. Methods

2.1. Materials

Cornstalk power (20–80 mesh) was used as raw material, which was dried in an oven at 105 °C for 24 h and kept in a desiccator at room temperature before use. Polyethylene glycol (PEG, M_n, 400) and glycerine were used as liquefaction solvents in the alcoholysis of cornstalk; 98 wt.% sulfuric acid was used as catalyst; 1,4-dioxane was used as solvent to dissolve the liquefied products and in determining the residue content. All these chemicals were of analytical reagent grades, which were obtained from commercial sources, and used without further purification.

2.2. Liquefaction of cornstalk

The liquefaction was carried out in a three-neck flask equipped with a stirrer, refluxing condenser and thermometer. The flask charged with the mixture of liquefaction solvents (PEG/glycerine, 4/1, w/w) and sulfuric acid (3 wt.%) was immersed into an oil bath and preheated at certain temperature. Quantitative cornstalk (liquid/solid, 10/3, w/w) was then added to the flask under stirring. The liquefaction was conducted under constant stirring and reflux at the certain temperature. After the presetting time, the flask was immersed in ice water to quench the liquefaction reaction.

2.3. Measurement of liquefaction ratio

The resultant product was diluted with a large excess (about 20 times of liquefied product) of dioxane/water (80/20, v/v) binary solvents, which had been recommended as the universal diluent for liquefied biomass (Kurimoto et al., 1999; Yao et al., 1993, 1994), and stirred with a magnetic stirrer for more than 4 h. Thereafter the diluted resultant was filtrated using filter paper under vacuum to separate residue from the liquefied cornstalk. The insoluble residue was rinsed thoroughly with the dioxane/water binary solvents until colorless filtrate was obtained, and then dried in an oven at 105 °C to constant weight. The liquefaction ratio, which was defined as the percent weight of the dioxane soluble liquefied cornstalk to the total cornstalk charged and used as an index of the extent of liquefaction efficiency, was calculated as follows:

$$\text{Liquefaction ratio} \quad \alpha = \frac{W_0 - W}{W_0} \tag{1}$$

$$\text{Residue content} \quad 1 - \alpha = \frac{W}{W_0} \tag{2}$$

where W and W_0 were the weights of insoluble cornstalk residue, cornstalk sample before liquefaction, respectively.

3. Kinetic models

The components of cornstalk are complex, and therefore it is almost impossible to measure the liquefaction rate like an individual reaction because of the chemical complexity of liquefaction reaction. Furthermore, it is difficult to isolate an individual reaction and measure its rate when one takes into considering the chemical complexity of the heterogeneous reactions occurring during biomass liquefaction. Nevertheless, it is possible to measure the concentration of liquefied products as a function of time, and the amount of liquefied products formed may be modeled using apparent reaction rate constants which could provide a better understanding of overall reaction process. Thus it is desirable to get a physical model describing the liquefaction process of cornstalk in polyhydric alcohols in terms of the changes of liquefaction ratio occurring in the system.

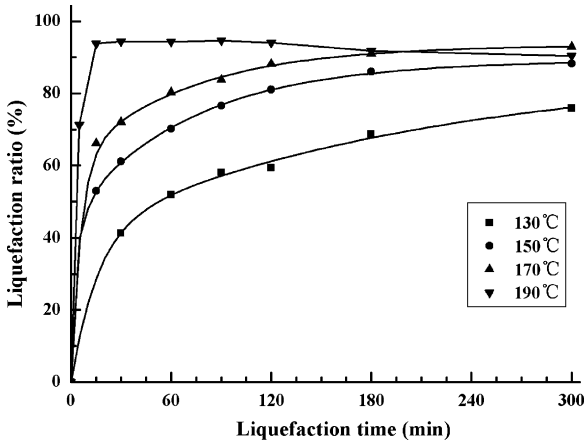

Fig. 1. Effects of reaction temperature on the liquefaction of cornstalk.

According to the previous studies about liquefaction reaction mechanisms (Lin et al., 1997a,b,c, 2001a,b; Pu and Shiraishi, 1993; Yamada and Ono, 1999, 2001; Yao et al., 1993), the liquefaction of biomass in organic solvents was a solvolysis process, and the solvents mainly solved and dispersed the liquefied products, and prevented the re-condensation of the degraded and modified components. On the other hand, the solvents in the liquefaction systems were more out and away than biomass, and so it could be seen that the solvents were superfluous. Thus for the liquefaction of cornstalk in this study, the concentration of polyhydric alcohols, which acted as liquefaction solvents, could be considered constant. And so the reaction rate was only in relation to the residue content, and the kinetic equation could be written as the follows:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{3}$$

In this equation, k was the apparent reaction rate constant, which measured up to the Arrhenius equation, $k = Ae^{-E/RT}$; $f(\alpha)$ was the liquefaction reaction function. It was assumed that $f(\alpha)$ was only in relation to the residue content $(1-\alpha)$ at any time, and not in relation to reaction temperature and other conditions. And so the liquefaction reaction function could be simplified as follows, $f(\alpha) = (1-\alpha)^n$, where n was the apparent reaction order. Therefore, the kinetic equation was taken as the following forms:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{4}$$

Thus, in association with Eqs. (1) and (2), the logarithmic form of the kinetic equation above was:

$$\ln\left(-\frac{1}{W_0}\frac{dW}{dt}\right) = \ln k + n\ln\left(\frac{W}{W_0}\right) \tag{5}$$

4. Results and discussion

4.1. Apparent reaction rate constant, reaction order and activation energy of the liquefaction of cornstalk

For the liquefaction of cornstalk, the liquefaction efficiency was influenced with liquefaction solvents, catalyst and its content, reaction temperature, reaction time, etc. (Kurimoto et al., 1999; Pu and Shiraishi, 1993; Yamada and Ono, 1999; Yao et al., 1993, 1994; Yan et al., 2008). The time-dependence of the liquefaction curves for cornstalk under different reaction temperatures is shown in Fig. 1. It could be seen that, with the increase of reaction temperature,