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Kinetic Study of Recycled Newspaper Liquefaction in Polyol Solvent

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Abstract The kinetics of liquefaction of recycled newspaper was investigated. Liquefaction was carried out in the presence of polyhydric alcohols and ethylene carbonate under acidic conditions. The liquefaction yield was found to be a function of the solvent type, sulfuric acid concentration, temperature, and the ratio of solvent to newspaper. The total liquefaction rate and degradation rates of cellulose, hemicelluloses, and lignin, which are the major components of newspaper, were measured. From the results, it was found that the total liquefaction rate did not follow first order reaction kinetics, because of the difference in the degradation rate of each component and the condensation of lignin. The degradation rates of lignin and hemicellulose were approximately 13 and 7 times greater than that of cellulose, respectively. © KSBB

Keywords: lignocellulosic biomass, liquefaction, polyhydric alcohol, reaction kinetics

INTRODUCTION

Nowadays, the price of fossil fuels and the amount of carbon dioxide generated are rapidly increasing due to the excessive use of fossil fuels. Therefore, a great deal of effort has been made to develop novel techniques to convert renewable resources into fuel and chemicals which can be used as substitutes for fossil fuels and their derivatives. One of these efforts involves lignocellulosic biomass, which is one of the most plentiful resources in the world, but whose utilization has been very limited because of the lack of processing techniques. The liquefaction of lignocellulosic materials is carried out in the presence of some organic solvents to produce polyurethane [1-4], epoxy resin [5], polyester [6], *etc.* Since this process is performed under atmospheric pressure, many advantages may exist for its commercial utilization. Polyhydric alcohols such as ethylene glycol (EG), polyethylene glycol (PEG), and glycerin are commonly used as solvents. Recent work [6,7] has shown that ethylene carbonate (EC) or propylene carbonate enhances the liquefaction rate when it is mixed with EG. The biopolymers produced from liquefied lignocellulosic material have been reported to be more biodegradable than petrochemical polymers [4], so they can be environmentally friendly materials.

The major components of lignocellulosic material are cellulose, hemicellulose, and lignin. Its liquefaction reactionwith an acid catalyst occurs in nonaqueous solvent, whereas its hydrolysis reaction with an acid catalyst is performed in an aqueous solvent. In EG liquefaction, cellulose and hemicellulose are degraded to low-molecular-weight materials and a considerable amount of EG-glucosides are produced [7]. Lignin produces free-radical fragments which are easily condensed in the presence of an acid [5]. EG can block the free-radical fragments and prevent the condensation of the fragments. Generally, hemicellulose is hydrolyzed in an aqueous solvent much faster than cellulose [8]. Considering these facts, the degradation rate of each component could be significantly different, which in turn would cause the liquefaction rate to change as the reaction proceeds. Up to now, one kinetic study of the liquefaction of corn stover has been reported [9]. In this study, the liquefaction process was assumed to follow first-order reaction kinetics, but it was found that this was not suitable, because the experimental values were significantly different from the predicted ones. This could be due to the different degradation rates of the various components, which have not been determined quantitatively yet.

Wastepaper is one of the most plentiful feedstocks and is relatively well recycled. It could be used as a raw material for bioethanol by hydrolyzing it enzymatically to glucose. However, it is not easy to increase the enzymatic digestibility due to the presence of ink and the other chemicals used in the pulping process [10,11]. In the case liquefaction, however, ink removal is not necessary. The major objectives of this study are to measure the liquefaction yield and the deg-

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radation rates of cellulose, hemicellulose, and lignin, which are the major components of newspaper. For this purpose, first, the liquefaction condition suitable for recycled newspaper was investigated.

MATERIALS AND METHODS

Materials

A mixture of recycled newspapers (Gyungnam Ilbo and Maeil Business Newspaper) was ground by IKA Labortechnik MF 10 cutting mill (Germany) with a 5 mm sieve insert. Its composition on an oven dry basis was 59.0% glucan, 16.2% hemicellulose, 12.4% kason lignin, and 5.8% ash. EG and EC (Fluka Co., Switzerland), PEG (Sigma Chemical Co., USA), and glycerin (Bio Basic Inc., Canada) were used as liquefying solvents. Sulfuric acid (Merck KGaA, Germany) and dioxane (Junsei, Japan) were used as catalyst and dilution solvent, respectively.

Liquefaction Reaction

Five grams of the substrate was placed in a 100 mL two-branched flask equipped with a stirrer and a reflux condenser. The mixture of liquefaction solvents and sulfuric acid was added in the flask. The concentration of sulfuric acid was calculated at wt (%) based on the amount of the mixed solvent. The liquefaction reaction was carried out under atmospheric pressure at 400 rpm in an oil bath for the desired time. After the reaction, the flask was immersed in cold water. The resulting reaction mixture was washed out into a beaker by 200 mL of a dioxane-water mixture (4/1, v/v), stirred for 4 h on a magnetic stirrer, and filtered using a Whatman no.1 filter paper. The residue was dried in a dryer at 104°C for 24 h. The liquefaction yield was determined by the following equation:

$$\text{yield} = 1 - (\text{weight of residue/weight of newspaper charged})$$

For the sugars and lignin analysis, the residue was rinsed again with 200 mL of a dioxane-water mixture to remove thoroughly the liquefied product contained in the residue and then dried.

Analysis

The solid residue was analyzed for sugars, klason lignin, and ash according to the NREL standard procedures [12]. Sugars were determined using an HPLC system which consisted of a Spectra System P1000 pump, Shodex RI-71 detector, and Bio-Rad HPX-87H column (conditions: 0.6 mL/min, 65°C, 0.005 M H_2SO_4). A PeakSimple Chromatography Data System (SRI Instruments, USA.) was used for data acquisition and analysis. All standard chemicals were purchased from Sigma Chemical Co. Since this system cannot resolve xylose, mannose, and galactose, their combined value was used and referred to as hemicellulose.

RESULTS AND DISCUSSION

Liquefaction Condition

The composition of the three major components of newspaper was 59.0 wt (%) cellulose, 16.2 wt (%) hemicellulose, and 12.4 wt (%) klason lignin. Newspaper is made mainly from softwood pulp and the lignin composition of softwood is 25~35 wt (%) on a dry basis. A significant amount of lignin is removed during the pulping process, so the relative cellulose content is increased. As the liquefaction condition, 3% sulfuric acid and 160°C were selected, which are commonly used in liquefaction. Also EG, EC, and PEG/glycerin were selected as the liquefaction solvents. Under acidic conditions, lignin degrades to free-radical fragments and their condensation occurs easily when the concentration of the degradation fragments is high. The condensation reaction takes place between the carbonium cations and electron-rich aromatic-ring carbons of the lignin compounds, leading to a diphenylmethane structure [7]. However, the hydroxyl group of polyhydric alcohols reacts with lignin and this reaction can block the free-radical fragments, thereby preventing the condensation of the fragments and inceasing the liquefaction yield.

In nonaqueous solvents, the acid potential of an acid catalyst is higher if the permittivity (dielectric value) of the solvent is higher [7]. Since the permittivity of EC is more than 2 times greater than that of EG, increasing the ratio of EC to EG can increase the liquefaction rate. However, EC produces carbon dioxide when it is transformed into EG at high temperature, causing a decrease of the liquefaction yield, due to the carbon loss through carbon dioxide emission [9]. In this study, EG and EC mixed solvents containing up to 20 wt (%) EC were used. Figure 1 shows the effect of the three different solvents on the liquefaction yield. The liquefaction yield for PEG400/glycerol (8/2) was slightly higher than that for EG/EC (9/1), but slightly lower than that for EG/EC (8/2). When the amount of EC in EG was increased, the liquefaction yield was increased. Thus, the ratio of EG/EC was selected as 8/2 for further experiments.

Generally, the liquefaction yield is increased when the solvent/newspaper ratio (w/w) is increased. A solvent/newspaper ratio of 3 to 1 has commonly been used for woody and herbaceous substrates. However, since the volume per mass of newspaper is much greater than that of these substrates, most of the liquid solvent at a ratio of 3 to 1 was absorbed by the newspaper and the dampened newspaper became attached to the reactor wall during the initial stage of the reaction. Consequently, it was very difficult to perform the reaction uniformly, particularly, at its initial stage. As shown in Fig. 2, the liquefaction yield increases as the solvent/newspaper ratio increases, but the difference in the yields decreases. Since the attachment of newspaper to the reactor wall was seldom observed at a ratio of 4 to 1, this ratio was selected for further experiments.

It is readily apparent that increasing the sulfuric acid concentration and reaction temperature will increase the liquefaction yield. Since the sulfuric acid used must be removed

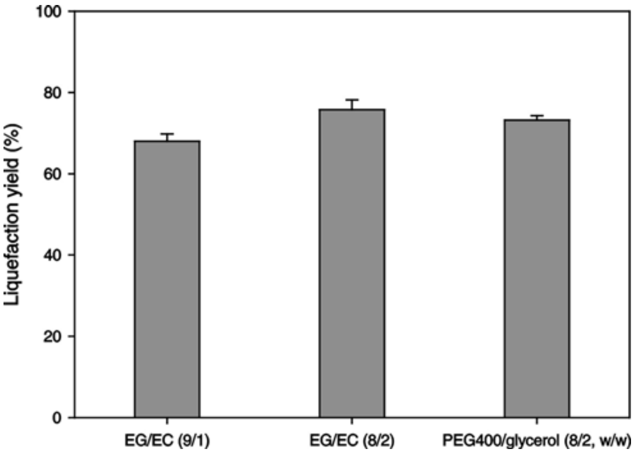

Fig. 1. Liquefaction yield of newspaper using different solvents. Solvent/newspaper ratio, 3; time, 120 min; EG, ethylene glycol; EC, ethylene carbonate; PEG, polyethylene glycol.

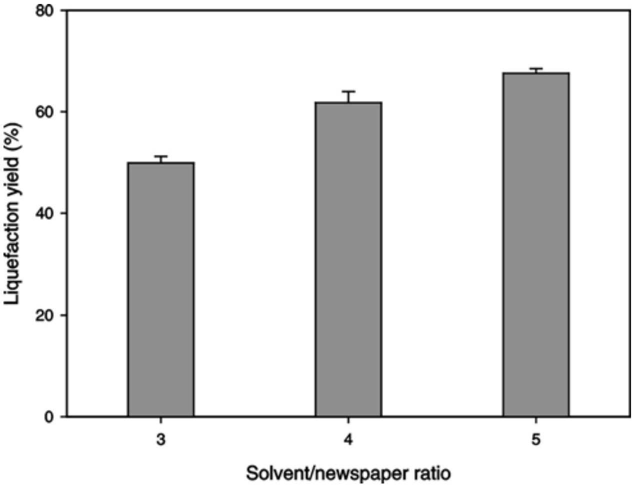

Fig. 2. Effect of the solvent/newspaper ratio on the liquefaction yield of newspaper. Solvent, EG:EC = 8:2; time, 60 min.

after the liquefaction process by a neutralization process and a high acid concentration accelerates the condensation of lignin as well as substrate liquefaction, 3% was selected after concentrations of 2~4% were tested (data not shown). Also, the effect of temperature was investigated in the range of 150~170°C. 160°C was selected, because further increasing the temperature resulted in less increase in the liquefaction yield (data not shown).

Liquefaction Rate

Figure 3 shows a comparison of the experimental liquefaction yield with the predicted yield. The liquefaction of newspaper took place rapidly at the initial stage and then gradually leveled-off. Assuming first order reaction kinetics, the reaction constant, k, was estimated using the experimental liquefaction yields and SAS NLIN program (version 8.0, SAS Institute Inc., USA). The predicted curve was presented as a solid line in Fig. 3. Here, liquefaction experiment was performed in duplicate and the results were presented as the average of two experiments with their standard deviations. As expected, the values predicted by the curve were lower than the experimental ones at the initial stage and higher after 60 minutes. This trend is very similar to the results reported by Yu *et al*. [9], who studied corn stover liquefaction with a 90% EG and 10% EC mixture solvent and assumed first order reaction kinetics for its liquefaction. Thus, it was thought that liquefaction did not follow first order reaction kinetics, but rather Michaelis-Menten kinetics which represents a simple enzyme-catalyzed reaction. The rate parameters for this equation were estimated using the SAS NLIN program and the predicted curve is presented as a dotted line in Fig. 3. This figure shows that the prediction by the Michaelis-Menten equation was in very good agreement with the experimental values, thus confirming again that the first order reaction kinetics is not suitable for expressing the liquefaction reaction.

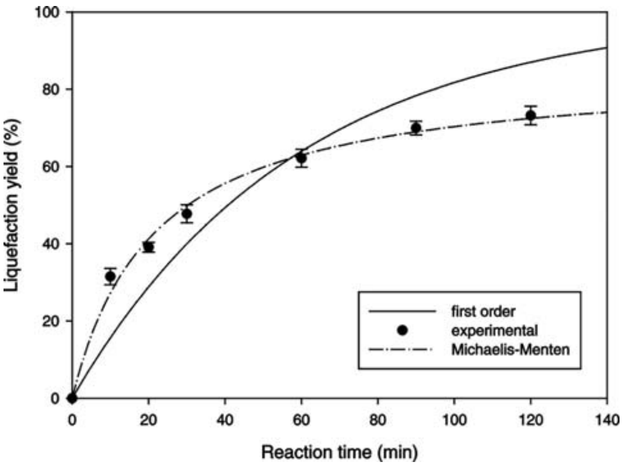

Fig. 3. Comparison of experimental liquefaction yield with predicted yield. Solvent, EG:EC = 8:2; solvent/newspaper ratio, 4.

To determine why the liquefaction reaction was not expressed by the first order reaction kinetics, but expressed well by the Michaelis-Menten reaction kinetics, the degradation rates of cellulose, hemicellulose, and lignin were measured. Figure 4 shows the residual content of each component after liquefaction. The degradation rate of cellulose was the lowest, with about 20% of it being left after 2 h of reaction. Hemicellulose was almost totally decomposed at 30 minutes and lignin was degraded by more than 80% at 10 minutes. The residual content of lignin did not change much after 10 minutes. Some researchers [5,7,13] reported that this would likely be due to the condensation reaction of lignin after measuring the total residual content, but they did not measure the residual lignin content. We confirmed this hypothesis by measuring the residual lignin content separately.

The degradation rates of cellulose, hemicellulose, and lignin were assumed to follow first order reaction kinetics. Figure 4

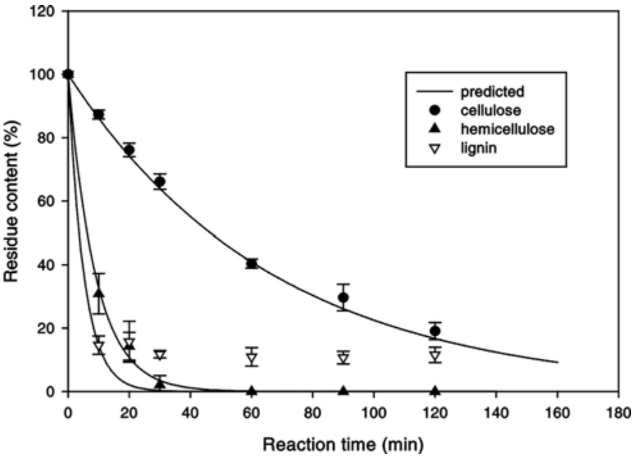

Fig. 4. Comparison of residual contents of cellulose, hemicellulose, and lignin with the values predicted by the first order reaction kinetics. Solvent, EG:EC = 8:2; solvent/newspaper ratio, 4.

Table 1. Rate constants for the liquefaction process of recycled newspaper

	k (/min)
Total residue	0.017
Cellulose	0.015
Hemicellulose	0.112
Lignin	0.192

shows that the predicted curves of cellulose and hemicellulose were in very good agreement with the experimental values and so each degradation rate can be expressed as a first order reaction. However, it is very difficult to fit all of the lignin data to the first order reaction curve, because of the condensation reaction of lignin. Since lignin condensate and lignin cannot be separately determined in the analytical method adopted here, a significant amount of lignin condensate should be included in the lignin values after 10 minutes. Hence, only the lignin value at 10 minutes was used to fit the first order reaction. Figure 4 shows that theoretically all of the lignin contained in newspaper could be degraded within 30 minutes.

Table 1 shows the rate constants for newspaper liquefaction when the liquefaction rate and degradation rate of each component were assumed to follow the first order reaction kinetics. Since the degradation rate of lignin or hemicellulose is approximately 13 or 7 times greater than that of cellulose, respectively, it can be said that newspaper consists of two different fractions, *i.e.,* the fraction easy to react and the fraction difficult to react. This means that the liquefaction reaction of newspaper can be fitted by either two-parallel first order reactions or a Michaelis-Menten type reaction, not a single first order reaction. The total liquefaction rate constant of newspaper is 0.017 min^{-1} at 3% and 160°C. This value is about 24% lower than the value of 0.021 min^{-1} obtained under the same acid concentration and temperature which were reported by Yu *et al*. [6]. However, this difference will be bigger, because their other conditions such as the ratios of solvent/solid and EG/EC are less favorable for liquefaction than our conditions. The high rate constant in their study for corn stover is probably due to its relatively high content of hemicellulose and lignin compared to newspaper [14].

CONCLUSION

The liquefaction of newspaper was conducted using three different organic solvents. The liquefaction yield varied with the solvent type, ratio of solvent to newspaper, temperature, and sulfuric acid concentration. We found that newspaper liquefaction does not follow first order reaction kinetics, because it consists of a fast fraction and slow fraction when the degradation reaction is carried out under an acid catalyst, and confirmed this by measuring quantitatively the individual degradation rates of cellulose, hemicellulose, and lignin.

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