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Reaction Kinetics of Stover Liquefaction in Recycled Stover Polyol

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Abstract

The purpose of this research was to study the kinetics of liquefaction of crop residues. The liquefaction of corn stover in the presence of ethylene glycol and ethylene carbonate using sulfuric acid as a catalyst was studied. It was found that the liquefaction yield was a function of ratio of solvent to corn stover, temperature, residence time, and amount of catalyst. Liquefaction of corn stover was conducted over a range of conditions encompassing residence times of 0–2.5 h, temperatures of 150–170°C, sulfuric acid concentrations of 2–4% (w/w), and liquefaction reagent/corn stover ratio of 1–3. The liquefaction rate constants for individual sets of conditions were examined using a first-order reaction model. Rate constant increased with the increasing of liquefaction temperature, catalyst content, and liquefaction reagent/corn stover ratio. Reuse of liquefied biomass as liquefying agent was also evaluated. When using recycled liquefied biomass instead of fresh liquefaction reagent, the conversion is reduced. It appeared that 82% of liquefaction yield was achieved after two times of reuse.

Index Entries: Corn stover; ethylene carbonate; ethylene glycol; liquefaction; polyol.

Introduction

About 80 million acres of corn are planted each year in the United States resulting in an estimated 120 million dry tons of corn stover. Additional agricultural byproducts/waste products available across the United States each year include an estimated 95 × 10^6 t of agricultural waste and 100–280 × 10^6 t of forest waste. Corn stover consists of the stalks, leaves, and cobs after the corn kernels are harvested. More than 90% of the stover is left in the fields. Less than 1% of corn stover is collected for industrial processing. About 5% is baled for animal feed and bedding. Much of the remaining 90+% must be plowed. The plowing operation can cause organic carbon and nitrogen

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losses because of oxidation, and increase the amount of fertilizer chemicals that need to be applied. The decay of the stover increases the release of CO_2, a greenhouse gas. Although some residue is required to protect the soil from erosion, most residues can be safely taken out of the fields for valuable utilization, which has the potential to be a win-win situation for the producer, processor, and the environment.

A number of studies have been performed on the effective utilization of crop residues and byproducts *(1–4)*. Liquefaction of biomass, also called solvolytic reaction, is one of the effective ways to produce valuable fuels and polymer materials. In the liquefaction process, crop residues are liquefied in the acidic conditions with liquefying reagents, such as ethylene glycol and ethylene carbonate. As a result, hydroxyl groups are introduced into the product. Some polyester, polyurethane or fuels have been prepared from the liquefied polyol product *(5,6)*. Yamada *(7)* reported that liquefaction of lignocellulosic biomass can be done in the presence of ethylene carbonate using acid catalysts at temperatures of 120–180°C. Heitz *(8)* have investigated the solvolytic power of some organic solvents such as aliphatic alcohol, polyols, phenol, lactic acid, and ethanolamine within the liquefaction process. Yao *(9)* focused his work on hydrolytic reactions of depolymerization in the cellulosic chain in phenol and phenol derivatives. In the present article, the influence of various reaction conditions on the liquefaction of corn stover such as liquefaction time, liquefaction temperature, sulfuric acid concentration, and the corn stover to liquefying reagent ratio was investigated. The solubility limit was also evaluated in order to understand the role of temperature and time in complete solvolysis of corn stovers. A first-order reaction model was then used to fit the kinetic of corn stover liquefaction.

Material and Methods

Materials

Air dried corn stover provided by Agricultural Utilization Research Institute was milled and then screened, and only the fraction less than 1 mm sieve was used in this research. Ethylene carbonate and ethylene glycol (Sigma, Minneapolis, MN) were used as liquefying reagents. Sulfuric acid (Sigma, Minneapolis, MN) was used as the catalyst.

Liquefaction Procedures

The liquefaction reaction was carried out in a 500-mL separable three-branch flask equipped with a stirring system and a reflux condenser in a mantle heater. After the desired reaction time, the heater was turned off, and the stirrer kept running until the mixture cooled down. At the end of liquefaction, the reactant was diluted by 200-mL dioxane-water solution (4/1, v/v) and then filtrated through filter paper under vacuum. The residue was dried to a constant weight at 105°C. The liquefaction yield was calculated by the following equation:

$$\text{Liquefaction yield} = \left(1 - \frac{\text{weight of dried residue}}{\text{weight of starting biomass}}\right) \times 100$$

The effects of following variables on liquefaction were investigated: (1) type of solvent, (2) temperature, (3) time, (4) amount of catalyst, (5) ratio of biomass solid to solvent, and (6) number of recycling liquefied biomass. All experiments and analysis were performed in triplicate.

Results and Discussion

Effect of Organic Solvent

Liquefaction of corn stover varied substantially with the two different solvents used in this study (Fig. 1). Liquefaction yield for ethylene carbonate approached maximum level in 0.5 h whereas liquefaction using ethylene glycol was very slow and 15% the corn stover still remained unliquefied after 2.5 h. Many bubbles were observed during the liquefaction with ethylene carbonate, which can be attributed to carbon dioxide gas emitted as a result of reactions between ethylene carbonate and biomass. This would be undesirable if it gets out of control in large-scale production. It also decreases the liquefaction yield because of the carbon loss through carbon dioxide emission. In the subsequent experiments, mixed solvents containing 90% of ethylene glycol and 10% of ethylene carbonate was used to achieve a reasonable liquefaction yield in an acceptable time frame.

The difference in liquefaction efficiency between ethylene carbonate and ethylene glycol may be related to their dielectric value *(7)*. In our liquefaction process, the catalyst (sulfuric acid) was dissolved in organic solvents. The acid potential thus depends on the solvent's dielectric value. Because ethylene carbonate has a higher dielectric value than ethylene glycol, it is reasonable that liquefaction of corn stover was faster with ethylene carbonate than with ethylene glycol.

Effect of Liquefaction Time and Temperature

Figure 2 shows the effect of liquefaction time and temperature on liquefaction yield. It demonstrates that both time and temperature have a great influence on the liquefaction yield. Liquefaction of corn stover took place rapidly in the initial period and gradually leveled off. The liquefaction yield increased with increasing temperature and time. When the temperature is 160°C, the liquefaction yield became relatively high (91%) at 2 h, and a further increase in temperature and time resulted in a depressed increase in liquefaction yield. Additionally, the liquefaction curves exhibited an exponential trend. This reaction could therefore be regarded as first-order reaction. Furthermore, this figure shows that a satisfied liquefaction result can be obtained at 2 h and 160°C.

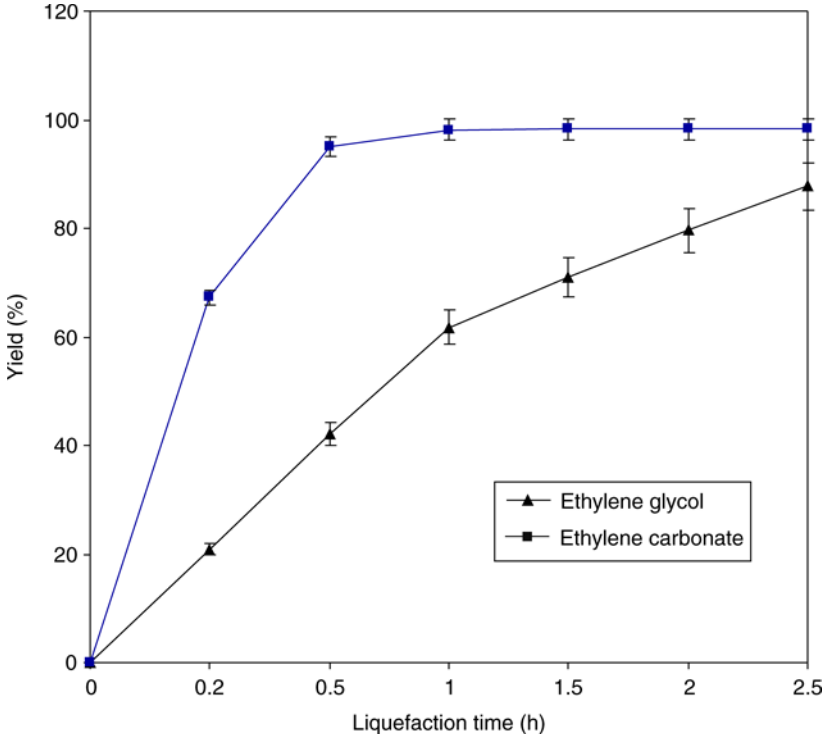

Fig. 1. Liquefaction of corn stover using different solvents. Liquefaction reagent/corn stover ratio, 3; catalyst content, 3% (w/w, on liquefaction reagent); temperature, 150°C; ▲, ethylene glycol; ■, ethylene carbonate. Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

Effect of Catalyst Content

The effect of the catalyst content on liquefaction is shown in Fig. 3. It is observed that the liquefaction yield increased with the increasing of sulfuric acid content. 92% liquefaction yield was obtained at 3% sulfuric acid in 2 h. We also attempted to substitute hydrochloric acid for sulfuric acid for economic considerations. After 2 h reaction at 6% hydrochloric acid, the liquefaction yield was only 54%, which is lower than the value obtained by the sulfuric acid catalyzed method. It indicated that sulfuric acid was better than hydrochloric acid, which may be because sulfuric acid is higher in acidity than hydrochloric acid. However, the use of sulfuric acid will cause condensation of degraded residues and increase the viscosity of the liquefied materials.

Effect of Liquefaction Reagent/Corn Stover Ratio

Figure 4 shows the effect of the liquefaction reagent/corn stover ratio on the liquefaction yield. The slope of the curve for ratio 3 is greater than it for ratios 1 and 2, indicating that the liquefaction reagent/corn stover ratio has a significant influence on the liquefaction yield. When the liquefaction

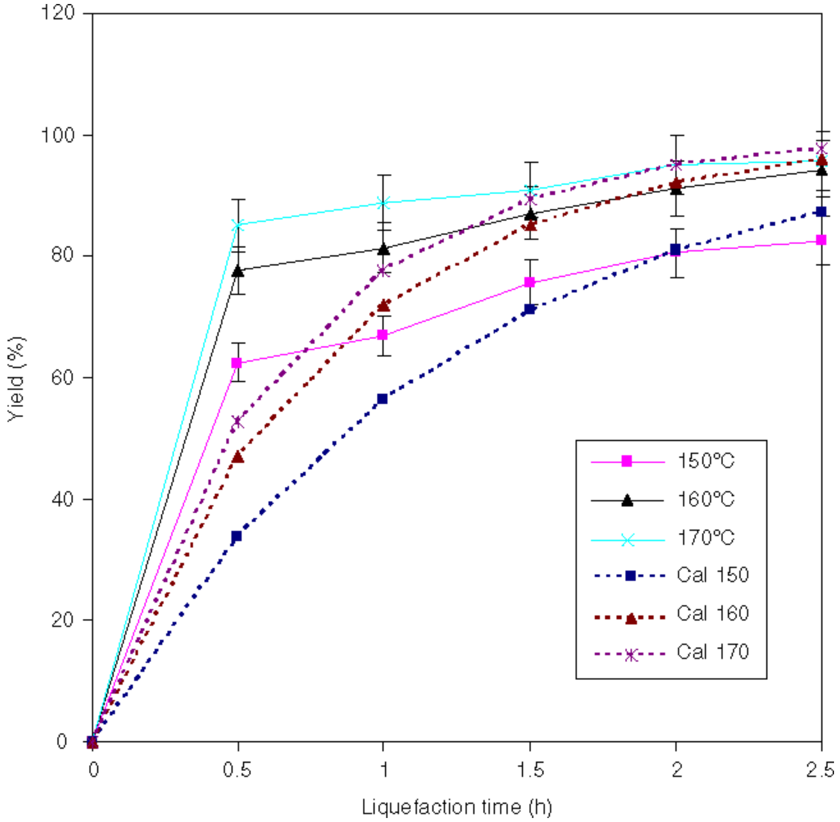

Fig. 2. Effect of time and temperature on the liquefaction of corn stover. Ethylene glycol 90% and 10% of ethylene carbonate acts as liquefaction reagent; liquefaction reagent/corn stover ratio, 3; catalyst content, 3%; liquefaction temperature: ■, 150°C; ▲, 160°C; ×170°C. Solid and dot curve represent the experimental and predicted curve respectively. Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

reagent/corn stover ratio reaches 3, the liquefaction yield is 91% after 2 h. A higher yield could be expected at even lower biomass loading but at the cost of a lower productivity. A ratio around 3 appears to be practical in our laboratory setting. A lower ratio may be possible and more economically viable in industrial scales.

Using Liquefied Biomass as Solvent

It would be economically important to recycle organic solvents in biomass liquefaction *(10,11)*. However, it is expensive to separate the solvents from the liquefied biomass. In this study, we tested the feasibility of using liquefied biomass as solvent, this based on the fact that the liquefied biomass is rich in hydroxyl groups, which is a characteristic of organic solvents for biomass liquefaction. Figure 5 shows the liquefaction yields as a function of number of times the liquefaction solvent was reused. Before

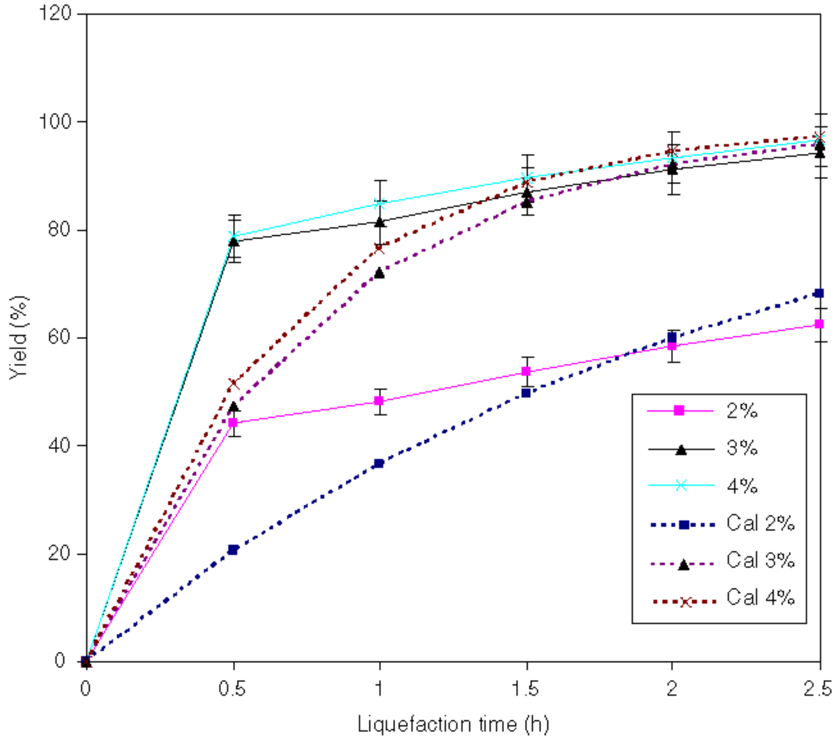

Fig. 3. Effect of the catalyst content on the liquefaction of corn stover. Ninety percentage of ethylene glycol and 10% of ethylene carbonate as liquefaction reagent; liquefaction reagent/corn stover ratio, 3; liquefaction temperature, 160°C; liquefaction time, 2.5 h; catalyst content: ■, 2%; ▲, 3%; x, 4%. Solid and dot curve represent the experimental and predicted curve respectively. Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

the reuse, the acidity of the liquefied biomass was readjusted to a sulfuric acid concentration of 3%. The result indicated that the liquefaction yield decreased with increasing number of reuse. The decrease in the yield may be attributed to: (1) decreased solvolytic capability of liquefied biomass, and (2) dramatically increased viscosity, which would limit reaction rates and present a challenge to mixing. We determined that 82% of liquefaction yield was achieved after two times of reuse.

Solubility Limit

Solubility limit (S_L) was used to describe the maximum concentration of corn stover dissolvable in liquefaction reagent. It had shown that S_L was 5% at 80°C and 12% at 100°C after 2 h liquefaction at 3% sulfuric acid (Fig. 6). The solubility limit is a construct that is valid only for steady-state conditions. It is likely to be a strong function of the ability of the cellulose to uncoil from its tight rigid rod configuration, which would explain the behavior near the glass transition temperature of approx 30°C. This uncoiling takes time, and as such the stovers require between 5 and 7 min becoming

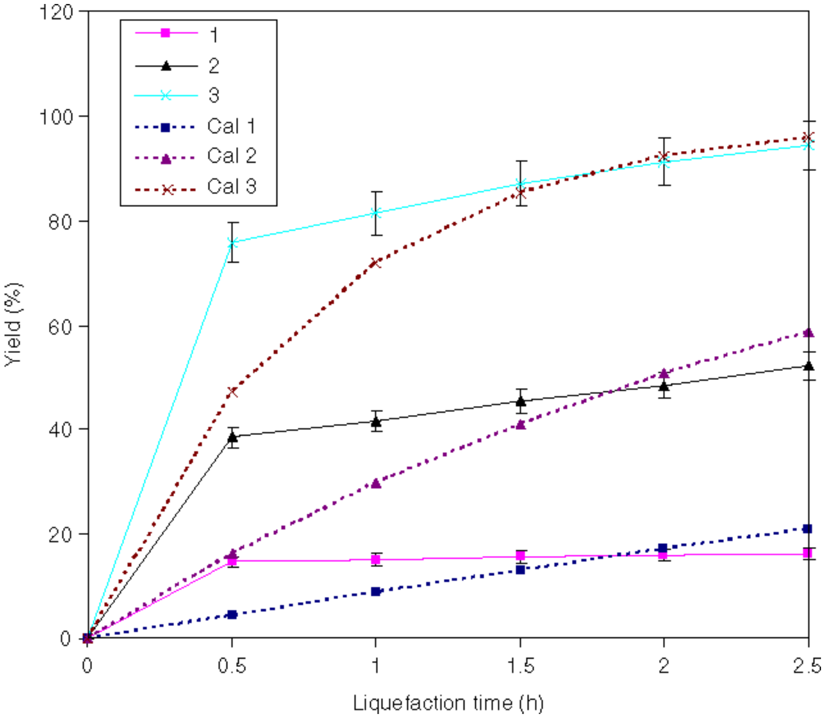

Fig. 4. Effect of the liquefaction reagent/corn stover ratio on the liquefaction of corn stover. Ninety percent of ethylene glycol and 10% of ethylene carbonate as liquefaction reagent; liquefaction temperature: 160°C; liquefaction time: 2.5 h; catalyst content, 3%; liquefaction reagent/corn stover ratio: ■, 1; ▲, 2; x, 3. Solid and dot curve represent the experimental and predicted curve respectively. Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

fully soluble in the polyol. At temperatures above 80°C, the S_L appears to increase almost linearly through the range studied.

The results presented in Fig. 2 suggest that 160°C was a desirable operational temperature, based on the high liquefaction yield and low unliquefied residue. For this, a starting point of 30% stovers in solution was tried. This is obviously far above what can be expected to react, as it quickly formed a solid mass. At 13 min, the system became more liquid-like, and at around 17 min was a stirred liquid system. This was likely the solubility limit, as shown in Fig. 7. A solubility limit S_L of 20% should be taken as maximum that can be expected to be in solution at any given time, and therefore the maximum that can react. For a fed system, in which the concentration is held constant, the feed rate would be set correspondingly. It was observed that slightly more stover can be present in the system, but at a risk of overloading, which could lead to interruption.

Solubility itself presents unique challenges. Solubility of the stovers in the polyol does not begin until approximately more than 80°C, in which a saturated solution forms a gel-like liquid–solid equilibrium. Cooling this quickly to less than approx 40°C causes the system to solidify, and slow

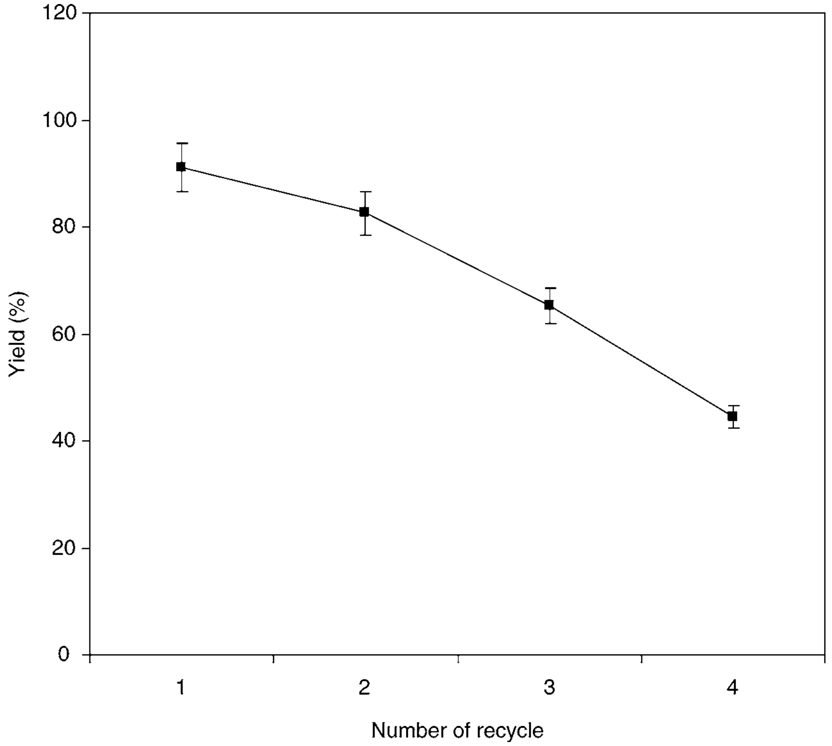

Fig. 5. Liquefaction rate of corn stover as a function of the recycle number. Liquefaction temperature, 160°C; liquefaction time, 2.5 h; catalyst content, 3%; recycled stover polyol/corn stover ratio, 3; Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

cooling allows the cellulose fraction to recrystalize out of solution. This may be a technique for purifying the cellulose/hemicellulose fraction.

First-Order Reaction Kinetics of Corn Stover Liquefaction

The liquefaction curves appeared to follow the first-order reaction. In a first-order reaction, the rate is proportional to the concentration of reactant of interest, which can be written as *(12)*

$$-\frac{\mathrm{d}[S]}{[S]} = k\mathrm{d}t \tag{1}$$

where S is the mass of corn stover, t the reaction time, and k a rate constant. Integrating Eq. 1 yields

$$\ln[S] = -kt + C \tag{2}$$

The constant of integration C can be evaluated by using boundary conditions.

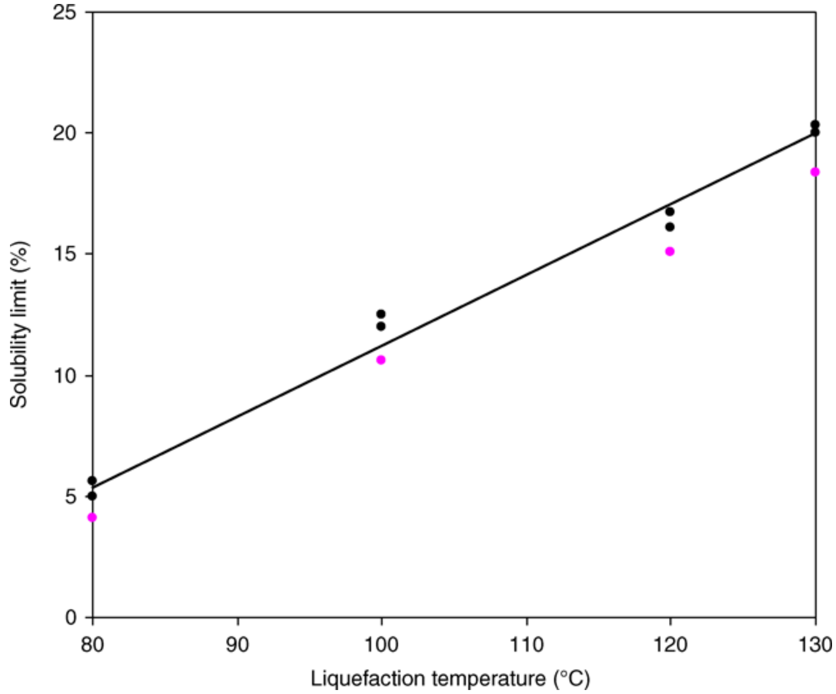

Fig. 6. Solubility limit of corn stover as a function of temperature. Ninety percent of ethylene glycol and 10% of ethylene carbonate as liquefaction reagent; liquefaction time, 2 h; catalyst content, 3%; corn stover content, 30%. Dots and solid line represent the experimental data and the predicted line, respectively.

When $t = 0$, $[S] = [S_0]$ where $[S_0]$ is the initial mass of reactant. Substituting into Eq. 2 gives the value of the constant of integration.

Finally an equation for the first-order reaction can be written as

$$\ln\frac{[S]}{[S_0]} = -kt \quad \text{or} \quad [S] = [S_0]e^{-kt} \tag{3}$$

The value of $[S]$ at different time t could be obtained from the experimental curves (Figs. 2–4). The rate constant k values for various parameters of the liquefaction processes were then calculated using Eq. 3 and shown in Table 1. The predicted curves for different liquefaction temperature, catalyst content and liquefaction reagent/corn stover ratio are presented in Figs. 2–4. Rate constant k increased with the increasing of liquefaction temperature, catalyst content and liquefaction reagent/corn stover ratio.

The average deviation is defined as

$$\text{deviation}\ (\%) = 100\frac{\sqrt{\sum([S]_i^{\text{exp}} - [S]_i^{\text{cal}})^2/N}}{[S]_{\text{max}}}$$

where N is the number of data points and $[S]_{\text{max}}$ is the maximum value of experiment data, subscript i refers to the data points used, $[S]^{\text{exp}}$ represents

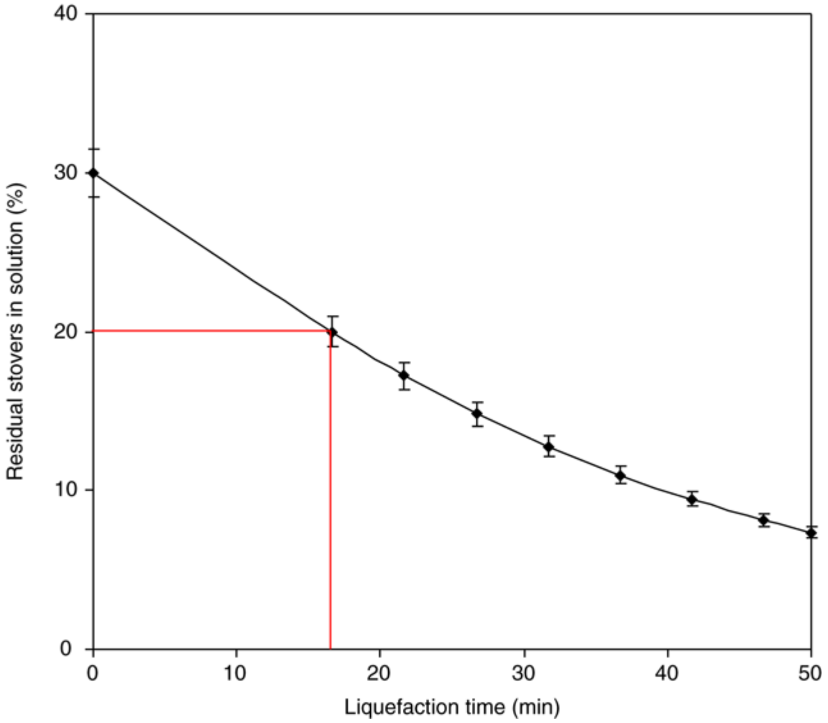

Fig. 7. Solubility limit of corn stover as a function of time. Ninety percent of ethylene glycol and 10% of ethylene carbonate as liquefaction reagent; liquefaction temperature: 160°C; catalyst content, 3%; corn stover content, 30%. Error bars represent standard deviations calculated from the data obtained from three duplicated experiments.

Table 1
k-Value for Liquefaction Process

		k (/h)	Deviation (%)
Temperature (catalyst = 3% sulfuric acid and ratio of solvent to biomass = 3)	150°C	0.83	15.4
	160°C	1.27	13.9
	170°C	1.50	14.6
Catalyst (temperature = 160°C, ratio of solvent to biomass = 3)	2%	0.46	17.8
	3%	1.27	13.8
	4%	1.45	12.0
Liquefaction reagent/corn stover ratio (temperature = 160°C, catalyst = 3% sulfuric acid)	1	0.09	32.7
	2	0.35	20.8
	3	1.27	13.1

the observed values and $[S]^{cal}$ represents those calculated by Eq. 3 for a given set of parameters. The experimental results were then described by the first-order reaction with an average deviation about 12–33% calculated in Table 1.

Conclusions

Liquefaction of corn stover was investigated in this study. The liquefaction yields varied with type of solvent, ratio of biomass solid to solvent, temperature, and type and amount of catalyst. Our research indicated that ethylene carbonate was better than ethylene glycol. Liquefaction yield increased with increasing ratio of solvent to biomass solid. A ratio around 3 was preferred for productivity and economical reasons. Liquefaction yield also increased with increasing temperature in the range from 150°C to 170°C. It was found that sulfuric acid was a better catalyst than hydrochloric acid for the liquefaction. Almost 3% of sulfuric acid was considered a practical catalyst concentration for our systems. The use of liquefied biomass as solvent was studied. It was found the liquefied biomass was not a good solvent; however 82% of liquefaction yield was achieved after two times of reuse. A first-order reaction model was used to explain the kinetic of corn stover's liquefaction with 12–33% deviation of prediction.

References

1 Rustamov, V. R., Abdullayev, K. M., and Samedov, E. A. (1998), *Energy Conversion Manag.* **39,** 869–875.
2 Flachowsky, G., Ochrimenko, W. I., Schneider, M., and Richter, G. H. (1996), *Animal Feed Sci. Technol.* **60,** 117–130.
3 Gorhmann, K., Torget, R., and Himmel, M. (1985), *Biotechnol. Bioeng. Symp.* **15,** 59–80.
4 Jackson, M. G. (1977), *Animal Feed Sci. Technol.* **2,** 105–130.
5 Karunanandaa, K. and Varga, G. A. (1996), *Animal Feed Sci. Technol.* **61,** 1–16.
6 Montane, D., Farriol, X., Salvado, J., Jollez, P., and Chornet, E. (1998), *J. Wood Chem. Technol.* **18,** 171–191.
7 Yamada, T. and Ono, H. (1999), *Biores. Technol.* **70,** 61–67.
8 Heitz, M., Brown, A., and Chornet, E. (1994), *Can. J. Chem. Eng.* **72,** 1021–1027.
9 Yao, Y., Yoshioka, M., and Shiraishi, N. (1994), *J. Appl. Polym. Science.* **52,** 1629–1636.
10 Rezzoug, S. A. and Capart, R. (2002), *Appl. Energy* **72,** 631–644.
11 Rezzoug, S. A. and Capart, R. (2003), *Energy Conversion Manag.* **44,** 783–794.
12 Sharma, R. K., Yang, J., Zondlo, J. W., and Dadyburjor, D. B. (1998), *Catalysis Today* **40,** 307–320.