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ORIGINAL ARTICLE

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Characterization of the products resulting from ethylene glycol liquefaction of cellulose

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Abstract The composition of liquefied cellulose in the presence of ethylene glycol (EG) was studied. The liquefied products were fractionated and analyzed with high-performance liquid chromatography and nuclear magnetic resonance. EG-glucosides were detected as the only saccharides and 2-hydroxyethyl levulinate as the highly decomposed compound derived from cellulose. Quantitative analysis of the EG-glucosides and levulinic acid that comes from the levulinate shows the presence of the following mechanism in the EG-liquefaction of cellulose. First, cellulose is degraded and produces considerable amounts of EG-glucosides during the early stage of liquefaction. Then, when liquefaction is prolonged, the glucosides are decomposed, leading to a large quantity of levulinates.

Key words Liquefaction · Ethylene glycol · Wood · Cellulose · NMR

Introduction

Utilization of biomass resources has been gaining importance in environmental protection. In 1995 the Japan Wood Research Society discussed "from fossil resources to wood resources" and suggested that we need to move toward a system that is nondamaging to the environment and that emphasizes renewable resources.[1] Many techniques have been developed for using biomass resources effectively. Wood liquefaction is one of those techniques for converting lignocellulosics into useful liquid materials.

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Since woody substances were converted to liquid materials by Fierz-David,[2] numerous studies have been reported on the liquefaction of lignocellulosics.[3] Their primary objectives have been to prepare liquid fuels. Liquefaction requires large quantities of energy, however, and the yield of liquefied products is not high.

Recently, this technique has been improved so whole lignocellulosics can be completely liquefied without producing residues. Ono and Sudo patented a method for preparing liquid materials that could be used as a raw material for adhesives by treating lignocellulosics with phenol in the presence of sulfuric acid.[4] Shiraishi et al. adopted polyhydric alcohols such as polyethylene glycol (PEG) and glycerin as liquefying reagents and liquefied lignocellulosics almost completely in the presence of an acid catalyst at approximately 150°C under atmospheric pressure.[5] During these treatments lignocellulosics can be converted to substances soluble in widely used organic solvents such as methyl alcohol, acetone, and dioxane. This technique, called liquefaction, has been studied vigorously since the early 1990s in Japan. Polyurethane resins can be prepared from the liquefied products with polyhydric alcohols in conjunction with isocyanates.[6] These polyurethane resins were expected to be biodegradable plastics.[7] The liquefaction techniques have not yet been industrialized. It is necessary to clarify the chemical characteristics of the liquefied products.

The behavior of lignin through liquefaction could be clarified from some studies of pulping using organic solvents as the pulping reagent (Organosolve Pulping). Hibbert and Rowley reported that lignin was leached out effectively when wood was treated with ethylene glycol (EG) and hydrochloric acid.[8] Nakano et al. reported that the hydroxy group of alcohol reacts with lignin at its α-position, and this reaction would prevent condensation of lignin during organosolve pulping.[9] Moreover, several studies on organosolve pulping using EG have been reported.[10,11]

On the other hand, there have not been many studies about the degradation of cellulose itself in organic solvents, although cellulose has been considered a useful raw material for factory products such as pulp and paper. A few

studies in this field lead us to further research on the degradation of cellulose.[12]

This paper describes the behavior of cellulose during liquefaction using EG (EG-liquefaction). EG was selected as the liquefying reagent because it is the most simple model compound for polyhydric alcohols. This study is the first step in characterizing the polyhydric alcohol liquefaction of lignocellulosics.

Materials and methods

Materials

A commercial cellulose from linter pulp (100–200 mesh; Toyo Roshi) was dried in vacuo and used for the model reaction of cellulose. Sawdust of white birch (*Betura Platyphylla* Sukatchev var. *japonica* Hara) wood meal (30–80 mesh) was obtained from several sawmills and used as lignocellulosics. It was dried in an oven at 105°C for 12 h and kept in a desiccator at room temperature before use. All the other chemicals used were extra pure grade reagents in accordance with the Japanese Industrial Standard and were used as received.

Liquefaction of lignocellulosics

The liquefaction was carried out in a flask equipped with a stirrer and a reflux condenser. EG 20 g, 97% sulfuric acid 0.6 g (3 wt% for EG), and 4 g of lignocellulosics such as cellulose were placed in the flask. The flask was immersed in an oil bath preheated to 150°C to start the reaction with stirring at 400 rpm. After a preset time the flask was immersed in cold water to quench the reaction.

Measurement of residue content

The resultant was diluted by an excess amount of 80% 1,4-dioxane, which was recommended as a universal diluent for liquefied biomasses.[13] The diluted resultant was separated with a Toyo GA100 glass filter to give residue and filtrate. The residue was rinsed well with the dioxane and dried in an oven at 105°C for 24 h. The residue content is defined as the percent dry weight ratio of the dioxane insoluble substance to the total lignocellulosics charged. It is usually used as an index of the extent of liquefaction. The dioxane-soluble part was neutralized by aqueous sodium hydroxide. The liquefied products were obtained by removing the dioxane and water from the filtrate under reduced pressure at 30°–40°C.

Separation of liquefied cellulose

Figure 1 illustrates the fractionation procedure of the liquefied cellulose. The liquefied products were diluted by an excess amount of distilled water and then separated into water-soluble and water-insoluble parts using TOYO hardened filter paper (TOYO 4A). The water-insoluble portion was rinsed well with distilled water and then dried in an oven at 105°C for 24 h (fraction A). The water-soluble portion was extracted with two 300-ml portions of chloroform in a 2000-ml separating funnel. The water was removed from the water layer with a rotary evaporator at 40°C under reduced pressure. The product was then dropped into an excess amount of dried ethyl alcohol. White precipitates formed in the solution and were identified as sodium sulfate with infrared spectroscopy. The sodium sulfate was filtered using TOYO hardened filter paper (TOYO 4A). Sticky substances were obtained by evaporating ethanol from the filtrate under reduced pressure (fraction C). The chloroform in the chloroform layer was removed with a rotary evaporator at 40°C under reduced pressure (fraction B).

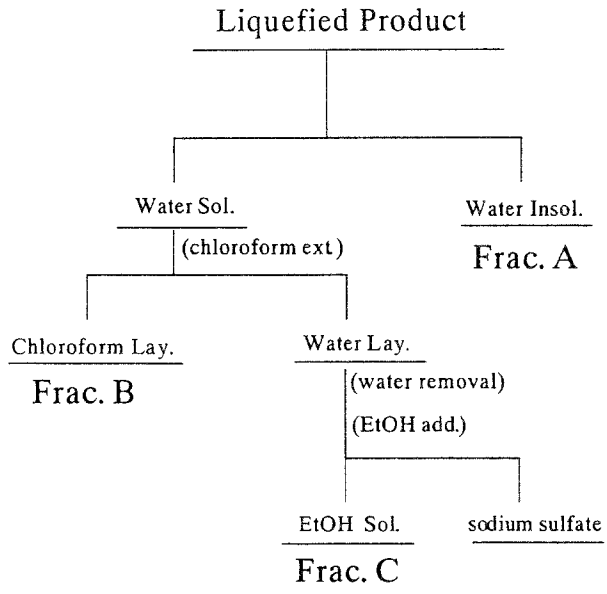

Fig. 1. Fractionation procedure for product separation

Saccharide analysis

The saccharides in fraction B were analyzed by high-performance liquid chromatography (HPLC). HPLC was performed using a Shimadzu LC-6A apparatus equipped with an amino column (Shodex NH2P-50). A chromatograms were monitored with a refractometer. A mixed solvent of acetonitrile and water (8:2, v/v) was used as the mobile phase, the flow rate of which was 0.5 ml/min. Quantification was done by external calibration curves based on peak areas from pure standards.

Organic acid analysis

Fraction B was placed in a 200-ml Erlenmeyer flask equipped with a reflux condenser and a magnetic stirrer. Distilled water (150 ml) and 97% sulfuric acid (0.2 g) were then added to the flask. The flask was refluxed on a hotplate with stirring. After a preset time, the flask was immersed in

cold water to quench the reaction. The organic acid content in the water solution was measured using the organic acid-measuring HPLC system.[14] The system was HP1100 (Hewlett-Packard) equipped with a column for organic acid analysis (Excelpak CHA-E11). $HClO_4$ (3 mM) was used as the mobile phase. Bromothymol blue (BTB) (0.1 mM) with 15 mM Na_2HPO_4 solution adjusted to pH 9.6 with aqueous NaOH was used as the reaction reagent. The reaction reagent was automatically added to the flow path at a point just after column separation to react with the eluted organic acids. The chromatograms were monitored with an ultraviolet (UV) detector at a wavelength of 445 nm. The flow rates of the mobile phase and the reaction reagent were both 0.6 ml/min. Quantification was done by external calibration curves based on peak areas from pure standards.

NMR measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL Lambda 400 spectrometer. The measurements were conducted in DMSO-d_6 at 27°C. ^{13}C-NMR spectra were recorded on the spectrometer at a frequency of 100 MHz using a complete decoupling, or DEPT (distortionless enhanced by polarization transfer), mode. For DEPT NMR a 135° pulse width of ^{1}H 16.2 μs was adopted.

Results and discussion

Liquefaction of cellulosics in the presence of EG

Figure 2 shows the residue content of cellulose and white birch wood as a function of the EG liquefaction time. The residue contents are plotted on a logarithmic scale. It is implied from Fig. 2 that the liquefaction followed the pseudo first-order reaction during the early stage. White birch wood is liquefied thoroughly within 180 min, whereas liquefaction of cellulose is slow. We have reported that cellulose is the most inaccessible wood component during the liquefaction of wood.[15] The low reactivity of cellulose could also be expected from existing research on organosolve pulping using EG.[10,11]

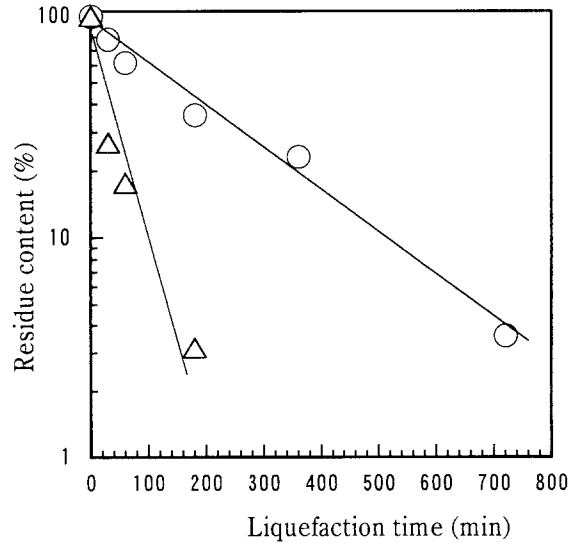

Fig. 2. Residue content of cellulose (*circles*) and white birch wood (*triangles*) as a function of the ethylene glycol (EG) liquefaction time

Characterization of fraction C

It is estimated that the EG liquefied cellulose contains the following compounds: saccharides derived from cellulose, highly decomposed nonsaccharide substances, EG, polymerized EGs (PEGs), and H_2SO_4 catalyst. Therefore, the liquefied products were fractionated according to Fig. 1 to obtain the saccharide-rich fraction (fraction C) for characterizing the structure of saccharides in the liquefied products.

Figure 3a shows the ^{13}C-NMR spectrum of fraction C at 60 min of liquefaction. The spectrum revealed numerous signals in the range of 60–90 ppm. The methine carbon signals due to the pyranose unit of cellulose are normally observed in this range.[16] Moreover, the methylene carbon signals due to EG and its polymerized product (PEGs) have been observed in the same range.[17] These signals are distinguishable from those of the product using the DEPT 135 mode.

Figure 3b shows the DEPT 135 NMR spectrum of fraction C. In this spectrum positive signals indicate methine carbons, negative signals indicate methylene carbons, and no signals appear for quaternary carbons. There are many methylene signals due to EG derivatives in the range of 60–90 ppm. Moreover, there are some methine signals due to the pyranose structure of saccharides. This spectrum suggests that saccharides remain in the EG-liquefied products at 60 min of liquefaction. Interestingly, there is no signal due to β-glucoside-bonded C1 carbon in the range of 103–110 ppm, except for the signal at 103.1 ppm due to the C1 position of 2-hydroxyethyl-β-D-glucopyranoside (described

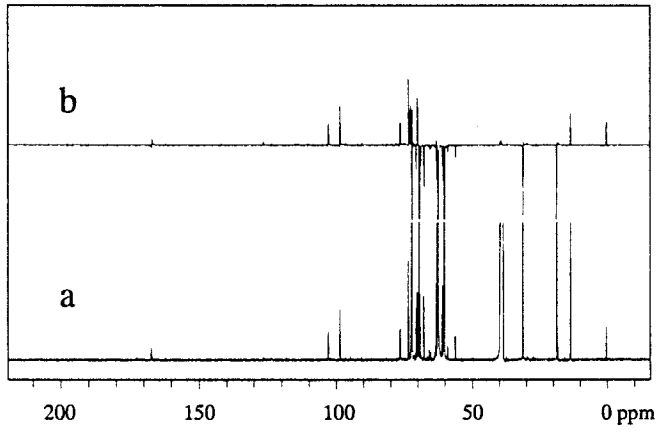

Fig. 3. ^{13}C-nuclear magnetic resonance (NMR) spectrum of (**a**) fraction C and (**b**) its distortionless enhanced by polarization transfer (DEPT) 135 NMR spectrum at 60 min of liquefaction

later). Normally, polysaccharides and oligosaccharides such as cellulose and cellobiose have a C1 signal in this range. These data suggest that fraction C contains mainly monomer saccharides.

HPLC analysis of fraction C

Figure 4 shows the HPLC profile of fraction C. The highest peak, at 10.1 min, is due to EG; and several peaks that appeared before 10.1 min are due to water or PEGs. The peak at 16.1 min is due to saccharides. Therefore, this 16.1-min peak was separated and characterized using NMR spectroscopy. Table 1 shows ^{13}C-NMR chemical shifts of the compound eluted at 16.1 min. The substances are identified as the EG-glucosides: 2-hydroxyethyl-α,β-D-glucopyranoside (Fig. 5a). The above results show that cellulose is degraded to monomer glucoside during EG liquefaction. The ratio of α and β compounds of the EG-glucosides was measured using NMR at the C1 position of the proton value. The α/β ratio is 66:34. The larger value of α compound would be caused by the anomeric effect.[18]

Table 2 shows the EG-glucoside content in the EG-liquefied cellulose. The percentages are calculated based on the theoretical EG-glucoside content that is calculated from the glucose unit number in the liquefied products. As shown in Table 2, the EG-glucoside content increased rapidly at the initial stage of liquefaction and reached 1012.6 mg at 60 min of liquefaction. The content then gradually decreased as the liquefaction time was prolonged, although the yield of the liquefied cellulose increased with liquefaction time. Moreover, the percentage of EG-glucosides in the liquefied cellulose decreased gradually with liquefaction time and reached only 1.92% at 720 min of liquefaction. These results suggest that the EG-glucosides are produced mainly at the initial stage of liquefaction and then change into other compounds as the liquefaction time is prolonged.

Characterization of fraction B

Figure 6 shows the ^{13}C-NMR spectrum of fraction B at 60 min of liquefaction. This spectrum presents sharp

Table 1. ^{13}C-NMR chemical shifts of ethylene glycol-α,β-D-glucopyranoside in DMSO-d_6

Position	δ (ppm)							
	C1′	C2′	C1	C2	C3	C4	C5	C6
α-Glucoside	69.0	60.0	98.7	72.0	72.6	70.2	73.3	60.8
β-Glucoside	70.6	60.2	103.1	73.4	76.4	69.9	76.8	60.9

Position is shown in Fig. 5a
NMR, nuclear magnetic resonance; DMSO, dimethylsulfoxide

Table 2. EG-glucoside content in EG-liquefied cellulose

Liquefaction time (min)	Liquefaction residue (%)	EG-glucosides	
		Amount[a] (mg)	%[b]
30	78.6	945.8	79.91
60	61.5	1012.6	47.49
180	35.8	792.8	22.31
360	23.2	459.3	10.81
720	3.6	102.4	1.92

EG, ethylene glycol
[a] Cellulose 4 g was charged at the EG liquefaction
[b] Percentages are calculated based on the theoretical EG-glucoside content calculated from the glucose unit number in the liquefied products

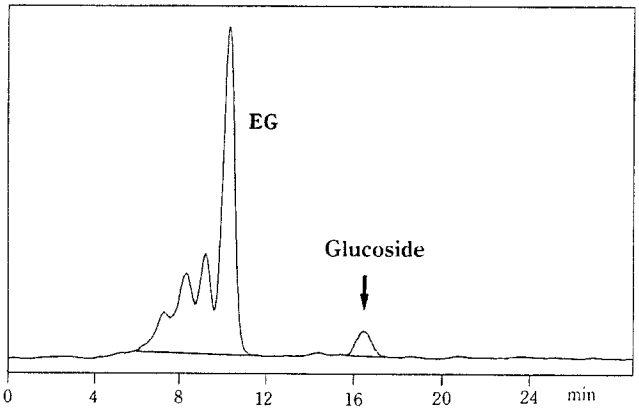

Fig. 4. High-performance liquid chromatography (HPLC) profile of fraction C at 60 min of liquefaction

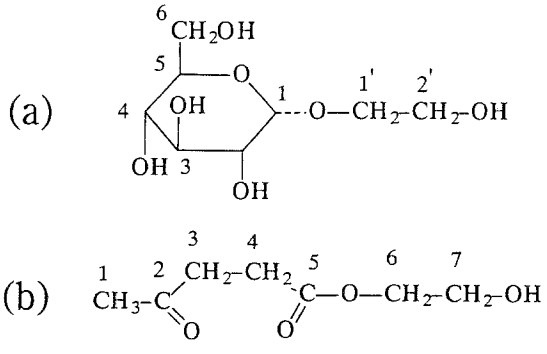

Fig. 5. Structures of (**a**) EG glucoside and (**b**) 2-hydroxyethyl levulinate

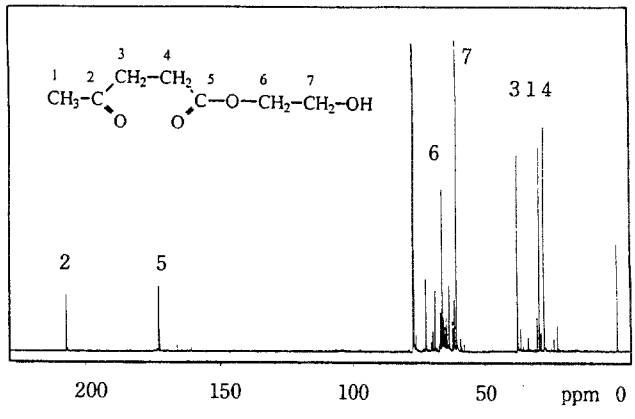

Fig. 6. ^{13}C-NMR spectrum of fraction B in $CDCl_3$ at 60 min of liquefaction

Table 3. ^{13}C-NMR chemical shifts of 2-hydroxyethyl levulinate in $CDCl_3$

Position	Chemical shift δ (ppm)
C1	29.8
C2	207.4
C3	38.0
C4	27.9
C5	173.1
C6	66.2
C7	60.8

Position is shown in Fig. 5b

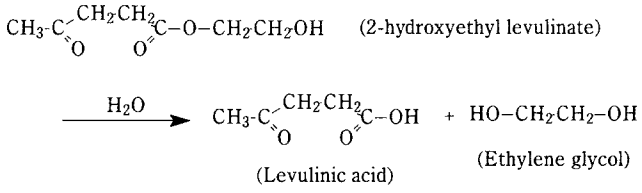

Fig. 7. Hydrolysis of 2-hydroxyethyl levulinate

signals due to levulinic acid structure with some methlene carbon signals due to EG derivatives. Moreover, it is confirmed that an EG bonds to the levulinic acid by forming ester linkage on two-dimensional NMR spectra. The ^{13}C-NMR chemical shifts of this levulinic acid EG ester (2-hydroxyethyl levulinate) are shown in Table 3. In general, levulinic acid is produced from glucose via hydroxymethylfurfural at high temperatures in aqueous acid medium.[19] In the case of EG liquefaction, it is suggested that glucosides are decomposed to the structure of levulininc acid, and levulinic acid is connected to EG simultaneously.

Determination of levulinic acid content in fraction B

Figure 7 shows the hydrolysis mechanism of 2-hydroxyethyl levulinate. Levulinic acid is easily isolated from 2-hydroxyethyl levulinate via acid-catalyzed hydrolysis. Fraction B was hydrolyzed with refluxing in 120 min to isolate levulinic acid completely, and the levulinic acid content is determined with the organic acid-measuring HPLC system. Figure 8 shows the HPLC profile of the hydrolysate from fraction B at 60 min of liquefaction. The peak eluted at 17.2 min is due to levulinic acid and the peak at 14.6 min to formic acid. Generally, formic acid is produced during levulinic acid production from hexose.[19] The formic acid found here would be a hydrolyzed product of formates. However, because the produced formic acid easily escapes the reaction system because of its low boiling point (100.5°C),[20] the formic acid value was not quantitated in this experiment. On the other hand, the levulinic acid peak can be calculated quantitatively on several liquefied products.

Table 4 shows the levulinic acid content and the weight of the water-insoluble fraction (fraction A) throughout the liquefaction. The percentages are calculated based

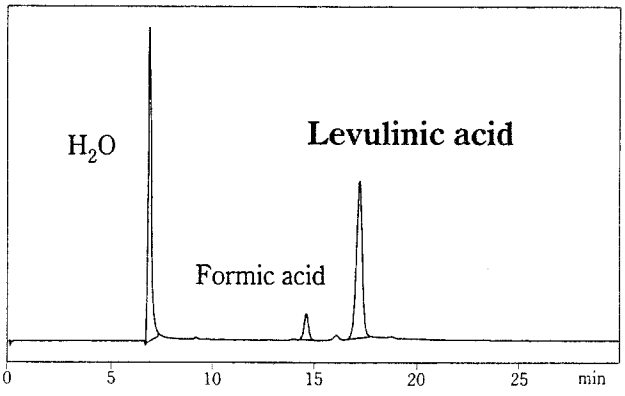

Fig. 8. HPLC profile of hydrolysate from fraction B at 60 min of liquefaction

Table 4. Levulinic acid content and weight of the water-insoluble fraction (fraction A) produced throughout liquefaction

Liquefaction time (min)	Levulinic acid		Fraction A[a] (mg)
	Amount[a] (mg)	%[b]	
30	41.0	6.69	36
60	163.9	14.85	17
180	509.0	27.66	164
360	649.4	29.52	249
720	732.7	26.54	469

[a] Cellulose 4 g was charged during EG liquefaction
[b] Percentages are calculated based on the theoretical levulinic acid content calculated from the glucose unit number in the liquefied products

on the theoretical levulinic acid content calculated from the glucose unit number in the liquefied products. As shown in Table 4, the levulinic acid content increased gradually with the liquefaction time and is more than 700 mg at 720 min. On the other hand, the percentage of levulinic acid fell slightly at 720 min of liquefaction owing to the gradually increasing fraction A with liquefaction time. The amount of fraction A increased to 469 mg at 720 min of liquefaction. The NMR analysis of fraction A shows that it does not contain any sugar substances. This fraction is estimated to be high-molecular-weight hydrophobic substances such as humin. Further analytical study is in progress.

Degradation mechanism of cellulose during EG liquefaction

Figure 9 shows the composition of the EG-liquefied products as a function of liquefaction time. The EG-glucoside content increases rapidly at the initial stage of the liquefaction; after 60 min of liquefaction the content then decreases gradually with liquefaction time. On the other hand, the levulinic acid content increases steadily with the liquefaction time instead of the EG-glucosides content. These findings indicate that the degradation of cellulose during EG liquefaction has the following mechanism: First, cellu-

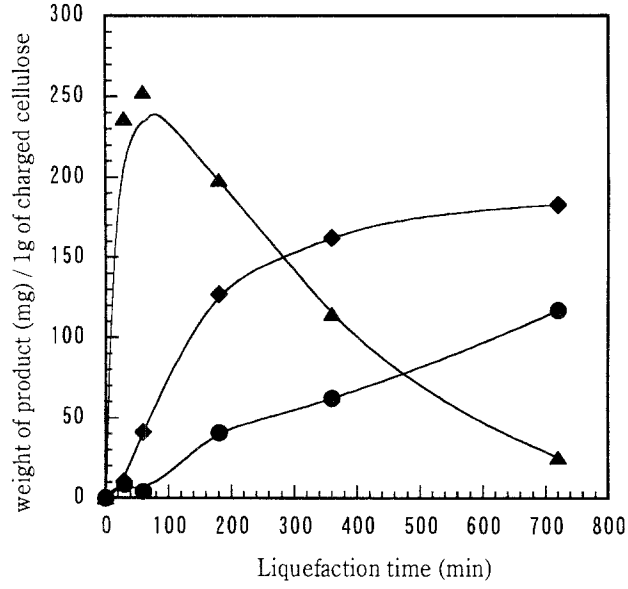

Fig. 9. Produced weight of EG glucosides (*triangles*) levulinic acid (*diamonds*), and fraction A (*circles*) based on 1 g of added cellulose as a function of the liquefaction time

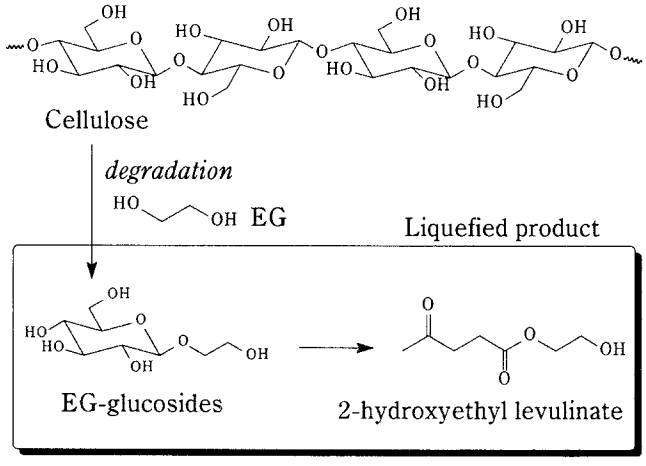

Fig. 10. Cellulose degradation mechanism during EG-liquefaction

lose is degraded and produces considerable EG-glucosides during the early stage of liquefaction. Second, when liquefaction is prolonged, glucosides are decomposed, leading to a large quantity of levulinates. This mechanism is illustrated in Fig. 10.

This mechanism suggests that the composition of liquefied products could vary depending on the liquefying condition. Therefore, it is important to control the reaction condition to produce a suitable composition for each application. The produced glucosides could be used as raw materials of some functional polymers, and levulinic acid from levulinates could be applied to the base material of some useful chemical products. The conversion of these liquefied products to useful chemical resources is now being studied.

Conclusions

Cellulose is liquefied in the presence of EG and an acid catalyst at elevated temperatures under atmospheric pressure. The logarithmic plots of the liquefaction curve suggest that EG-liquefaction of cellulose is following a pseudo first-order reaction during the early stage. A large quantity of α- and β-D-glucosides are detected at an early stage of EG-liquefaction. However, the glucosides are converted to 2-hydroxyethyl levulinate, when the liquefaction time is prolonged. These results suggest that the chemical composition of liquefied cellulose strongly depends on the liquefying condition.

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