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Chemical analysis of the product in acid-catalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate

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Abstract Degradation and decomposition of cellulose were studied in an acid-catalyzed solvolysis treatment of biomass using polyethylene glycol (PEG) and ethylene carbonate (EC). The solvolysis reaction was followed by a typical reaction system of wood liquefaction that uses sulfuric acid catalyst at 140° or 150°C at atmospheric pressure. The methods of fractionation and chemical analysis of the degraded cellulose in the solvolyzed product are discussed. The solvolyzed product was separated into several fractions, and they were hydrolyzed to release glucose and levulinic acid to determine the quantity of glucosides and levulinates in the solvolysis product. The data clearly showed that the solvolysis reaction had the same mechanism when using PEG or EC. Degradation of cellulose leads to the formation of glucosides, which then decompose, resulting in a levulinic acid structure, and producing a water-insoluble fraction. The conversion rates of both glucosides and levulinates strongly depend on the reaction conditions of the solvolysis. In particular, EC promotes faster conversion of the reactions. The method discussed here is a chemical analytical technique for characterization of the products of wood liquefaction.

Key words Cellulose · Ethylene carbonate · Polyethylene glycol · Solvolysis · Wood liquefaction

Introduction

Solvolysis has been applied as a useful technique for fractionation of wood components. Numerous researchers have investigated the development of a wood pulping technique for solvolysis using organic solvents such as methanol,^{1,2} ethanol,^{3,4} ethylene glycol,⁵ propylene glycol,⁶ and phenols.⁷ McDonough⁸ reviewed the degradation mechanism of lignin in solvolysis pulping. However, few studies have been reported on the drastic degradation of cellulose in solvolysis treatment, because cellulose should not be degraded in the pulping treatments. Recently, recycling of woody waste has attracted a great deal of attention due to environmental protection issues. In general it is preferable to reuse all woody waste, although some woody waste is of poor quality cannot provide cellulose that is suitable for paper production. Drastic solvolysis of cellulose could be a key point for biomass recycling.

In the early 1990s in Japan, research began in earnest on a solvolysis technique for chemically converting whole wood components into soluble materials.^{9–11} The goal was to prepare a raw material for resins such as plastic films,¹² molding materials,¹³ and adhesives.¹⁴ This technique is called “wood liquefaction.” Because the reaction conditions of wood liquefaction are severe, the quality of the cellulose in the biomass is irrelevant.¹⁵ Therefore, wood liquefaction has been studied as an advantageous method for recycling woody waste.

We have reported that wood liquefaction is defined as an excess treatment of solvolysis pulping.¹⁶ Solvolization of lignin and hemicellulose is much easier than that of cellulose. Because the degradation of cellulose is the most energy-consuming stage, accelerating the reactivity of cellulose is an important point of this technique.¹⁷

In the late 1990s, we found that cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) caused very rapid degradation of cellulose.^{18,19} The use of EC greatly improved the degradation speed, making it 27 times faster than that of conventional cellulose degradation. Normally, solvolysis reaction begins with lignin degradation

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and cellulose is the most resistant component to the reaction. However, in the case of EC, the reverse is true with the speed of cellulose degradation being apparently faster than that of lignin removal.¹⁸

An acid-catalyzed solvolysis reaction of cellulose in an autoclave using monoalcohols such as methanol and ethanol was discussed by Garvas.²⁰ On the other hand, we have studied solvolysis reactions under atmospheric pressure using high boiling point reagents. Our previous model reaction using ethylene glycol (EG) showed a clear mechanism of acid-catalyzed solvolysis producing EG glucosides and 2-hydroxyethyl levulinates.¹⁶ However, in the case of using polyethylene glycol (PEG), which is the most frequently used reagent in the wood liquefaction,¹² it is difficult to directly analyze the chemical composition of the solvolyzed products due to the poor separability of PEG. Even if EC is used, the situation will be the same because EC changes into a PEG structure during the reaction.¹⁸ To use this technique in industrial applications, it is necessary to develop a suitable chemical analysis method for the resultant product. In this study, a chemical analysis method for determination of the chemical composition of the solvolyzed product was studied. Because the degradation of cellulose is the key point for the drastic solvolysis of biomass described above, we focused on cellulose degradation as the first step of the study.

Materials and methods

Materials

A commercial α -cellulose (Sigma) was dried in vacuo and used as the test cellulose. Sawdust from Japanese cedar (*Cryptomeria japonica* D. Don) wood meal (30–80 mesh) was obtained from several sawmills and used as wood meal. It was dried in an oven at 105°C for 12 h and kept in a desiccator at room temperature before being used. All other chemicals used were extra pure grade reagents in accordance with the Japanese Industrial Standard (JIS) and were used as received.

Solvolytic reaction of cellulose

The solvolysis reaction was carried out in a flask equipped with a stirrer and reflux condenser. The flask contained a mixture of 5 g of a solvolysis reagent such as EC, EG, glycerin (Gly), or PEG400 (PEG with average molecular weight of 400). Then 0.15 g (3% w/w of the solvolysis reagent) of 97% sulfuric acid was added into the flask. One gram of cellulose such as cellulose and wood meal was then added to the flask and mixed well. The flask was immersed in an oil bath preheated at 140° or 150°C to start the solvolysis reaction. Every solvolysis reaction was carried out under atmospheric pressure. After a preset time, the flask was immersed in cold water to quench the reaction. The reaction mixture was diluted by about 80% with 1,4-dioxane.

The dioxane-diluted mixture was separated into residue and filtrate with an Advantec GA100 glass filter. The resi-

due content was defined as the percentage dry weight of 80% 1,4-dioxane-insoluble substance to the total cellulose charged.²¹ The dioxane-soluble content was calculated by the residue content and defined as a degree of solvolysis reaction. The filtrate was neutralized with 1 N sodium hydroxide solution. The solvolyzed product was obtained by the removal of dioxane and water from the filtrate with a rotary evaporator under reduced pressure at 30°–40°C.

Separation procedure for solvolyzed product

Figure 1 shows a scheme of the separation procedure for the solvolyzed product analysis. The solvolyzed product was diluted with excess distilled water, and then separated into water-soluble and water-insoluble parts with an Advantec 4A hardened filter paper. The water-insoluble part was well rinsed with distilled water and then dried with a vacuum dryer at room temperature for 72 h. The water-insoluble fraction content was defined as the percentage dry weight of water-insoluble substance to the total cellulose that were added. The water-soluble part was transferred to a separating funnel and was extracted with chloroform (200 ml \times 8).

Chemical analysis of the chloroform layer

Chloroform in the chloroform layer was removed by rotary evaporation under vacuum at 30°C. The residue was then transferred to a flask equipped with a reflux condenser and a magnetic stirrer bar. Water (80 ml) and 0.1 mg of 97% sulfuric acid were added to the flask. The flask was refluxed

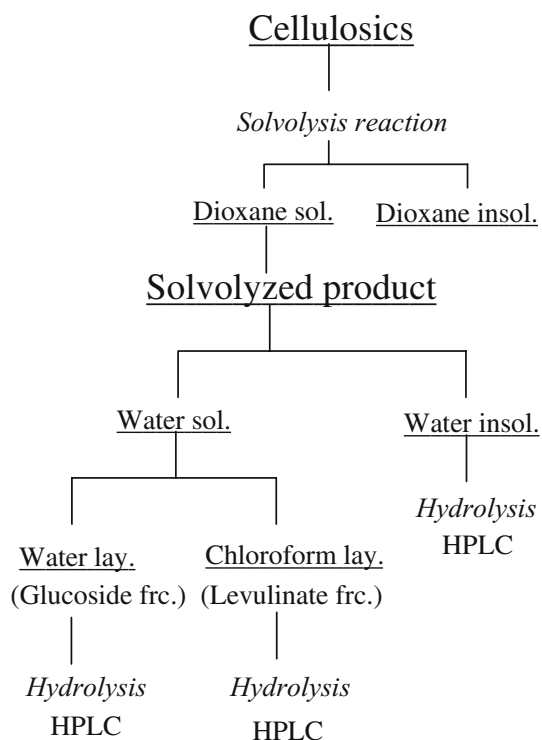


Fig. 1. Fractionation procedure for the solvolyzed product analysis

for 150 min at 100°C with stirring to separate levulinic acid from levulinates. The levulinic acid content was determined by high performance liquid chromatography (HPLC).

Chemical analysis of the water layer

The water layer was concentrated by rotary evaporation under reduced pressure at 40°C. The residue was transferred into a glass tube that was equipped with a Teflon packing cap. Sixty milligrams of 3M tetrafluoroacetate (TFA) was added to the tube, which was then sealed tightly and immersed in an oil bath preheated at 100°C for 4h. After a preset time, the tube was immersed in cold water to quench the reaction. The solution inside the tube was transferred to a flask and TFA was removed under reduced pressure at 40°C using a rotary evaporator. The glucose content in the resultant solution was then analyzed by HPLC with a sugar analysis column.

Chemical analysis of the water-insoluble fraction

The water-insoluble residual fraction might have contained a levulinic acid structure as a form of levulinates. The levulinate content was measured by the following hydrolysis procedure. The water-insoluble fraction was placed in a flask equipped with a reflux condenser and a magnetic stirrer bar. Water (80ml) and 0.1g of 97% sulfuric acid were then added to the flask. The hydrolysis reaction was carried out at 100°C under reflux with stirring for 150min. After the reaction, the aqueous solution in the flask was analyzed by HPLC.

HPLC analysis for levulinic acid content

Levulinic acid content was determined with a special HPLC organic acid measuring system described previously.¹⁶ The solution was directly injected to the HPLC system and levulinic acid was detected selectively. The levulinic acid mole percentage was calculated as the amount of levulinic acid present relative to the theoretical value of levulinic acid production based on the added cellulose content.

HPLC analysis for glucose content

Glucose isolated from the water layer was analyzed by HPLC with a sugar analysis column. The HPLC analysis was performed using an Agilent HP100 system equipped with an amino column Shodex NH2P-50. The chromatograms were monitored with a refractometer. The mobile phase was a mixed solvent of acetonitrile and water (8/2, v/v), with a flow rate of 0.5ml/min. Quantification was achieved by comparison with external calibration curves based on peak areas from pure standard. The glucose mole percentage was calculated as the amount of glucose relative to the theoretical value of glucose production based on the added cellulose.

Results and discussion

Solvolytic of cellulose using PEG400

The solvolysis reaction of cellulose was studied using PEG400 as a solvolysis reagent at 150°C (Fig. 2). The dioxane-soluble content, which defines the degree of solvolysis reaction, increased with the solvolysis time and reached almost 100% after 60min. On the other hand, the water-insoluble fraction that separated from the solvolysed product increased at the late stage of the solvolysis. This fraction started to increase after 30min of reaction and then strongly increased with the solvolysis time after 60min of reaction.

The change of levulinic acid and glucose content as a function of the solvolysis time is shown in Fig. 2b. The glucose content was measured by using hydrolysis treatment with TFA to produce glucose from PEG glucosides that might exist in the solvolysed product. A lot of glucose was produced at the initial stage of the reaction. However, the amount of glucose decreased gradually with the solvolysis reaction and it almost disappeared after 120min of reaction time. On the other hand, the amount of levulinic acid

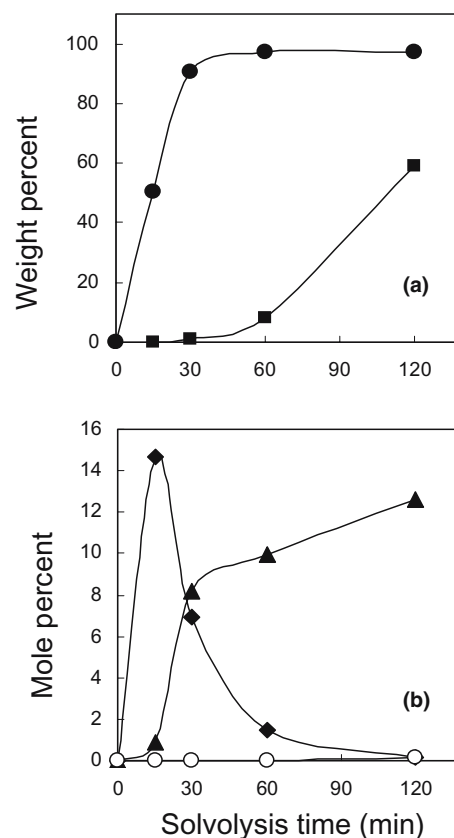


Fig. 2. **a** Solvolysis of cellulose using polyethylene glycol (average molecular weight 400; PEG400) and **b** chemical composition of the solvolysed products with solvolysis time. *Filled circles*, dioxane-soluble content; *squares*, water-insoluble content; *diamonds*, glucose; *triangles*, levulinic acid in the water-soluble fraction; *open circles*, levulinic acid in the water-insoluble fraction

strongly increased when the glucose content was decreasing, and then slowly increased as the solvolysis proceeded. The levulinic acid content in the water-insoluble fraction was not as high, but it increased with reaction time. These data suggest that the solvolysis reaction of cellulose proceeded with the following mechanism. First, cellulose degraded into glucose units; then this glucose was converted to levulinic acid as the solvolysis reaction proceeded.

Solvolysis of cellulose using EC

The solvolysis reaction of cellulose using EC as a solvolysis reagent at 140°C was studied (Fig. 3). Cellulose was converted into dioxane-soluble material after 20 min of the solvolysis reaction. The reaction rate was rather fast even though it was at a lower reaction temperature (140°C) than the solvolysis using PEG400 (150°C). We reported earlier that EC provides a drastic degradation of cellulose under acidic conditions.¹⁸ EC is a very effective reagent for the degradation of cellulose.

The amount of water-insoluble fraction increased with the reaction time. Interestingly, this fraction increased even at the initial stage of the reaction and the amount was somewhat higher than that for the process using PEG400. The behavior of glucose and levulinic acid formation using EC was similar to that observed when using PEG400.

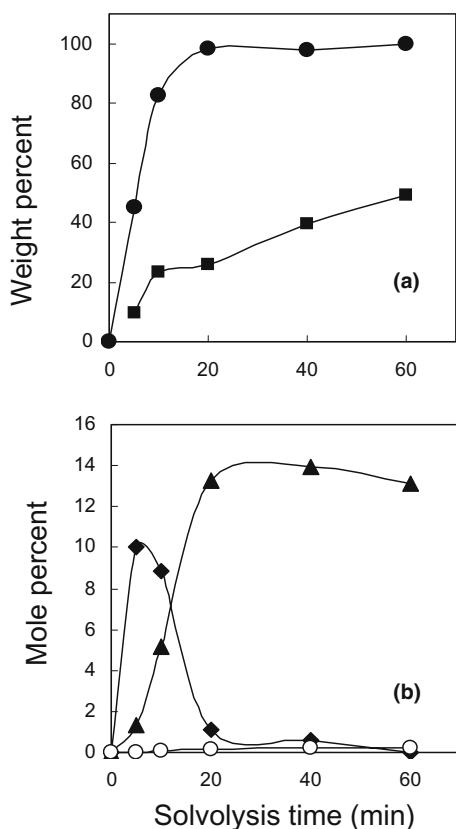


Fig. 3. **a** Solvolysis of cellulose using ethylene carbonate (EC) and **b** chemical composition of the solvolysed products with solvolysis time

Solvolysis of wood using PEG400/Gly system

The solvolysis reaction of wood using PEG400/Gly (7/3, w/w) as a solvolysis reagent at 150°C was studied (Fig. 4). Kurimoto et al.²² reported that the system using PEG400/Gly (7/3, w/w) led to excellent wood degradation, and this system is commonly used for wood liquefaction. Therefore, the data shown in Fig. 4 is the data for cellulose degradation during wood liquefaction.

The wood was thoroughly solvolysed after 60 min of the solvolysis (Fig. 4a). The water-insoluble fraction increased with the solvolysis time, and the amount was rather high even at the initial stage of the solvolysis reaction. This might have been due to lignin condensation during the solvolysis reaction under the acidic conditions. We previously reported that condensed residues contained many aromatic compounds, which infrared spectroscopy analysis suggested might have been caused by lignin condensation.²³

The trends in the formation of glucose and levulinic acid from wood were similar to those from cellulose (Fig. 4b). Glucose units were produced at the initial stage of the reaction, but they disappeared as the reaction progressed. On the other hand, levulinic acid content increased with the reaction time and leveled off at the late stage of the reaction. These data suggest that solvolysis of cellulose in wood follows the same mechanism as that for solvolysis of neat cellulose.

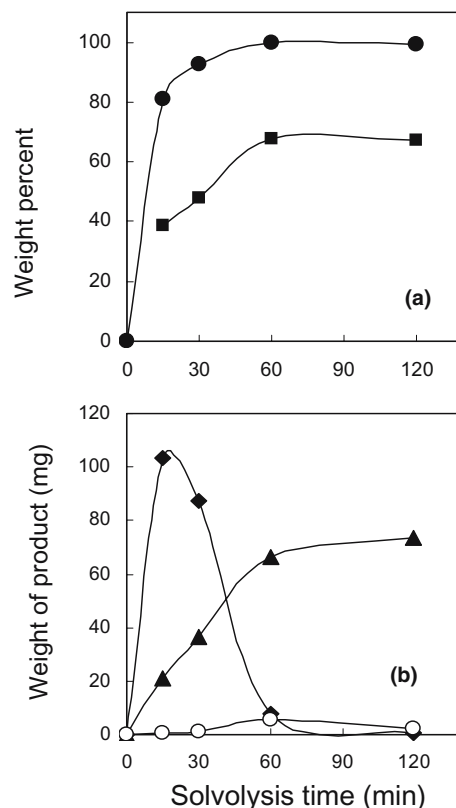


Fig. 4. **a** Solvolysis of wood using PEG400/Glycerin system and **b** chemical composition of the solvolysed products with solvolysis time

Solvolysis of wood using EC/EG system

Solvolytic of wood using EC/EG (8/2, w/w) as the solvolysis reagent at 140°C was studied (Fig. 5). We reported earlier that using 20% EG with EC prevented the formation of condensed residues and produced a 100% solvolyzed material with the rapid liquefaction of wood.¹⁸ As shown in Fig. 5a, the speed of solvolysis was faster than that using the PEG400/Gly system even though this reaction occurred at the lower reaction temperature of 140°C. The amount of the water-insoluble fraction showed a similar trend to that observed for the PEG400/Gly system; it increased with reaction time.

The behavior of glucose and levulinic acid formation using the EC/EG system was basically similar to that observed when using the PEG400/Gly system. However the total amounts of each of them using the EC/EG system were smaller than those from the PEG400/Gly system. This might have been due to the formation of the water-insoluble fraction. The water-insoluble fraction might include not only decomposed sugar derivatives, but also a lot of lignin; this is difficult to investigate. Moreover, the reactivity of lignin will vary according to the solvolysis reaction conditions. A study of the reactivity of lignin is in progress.

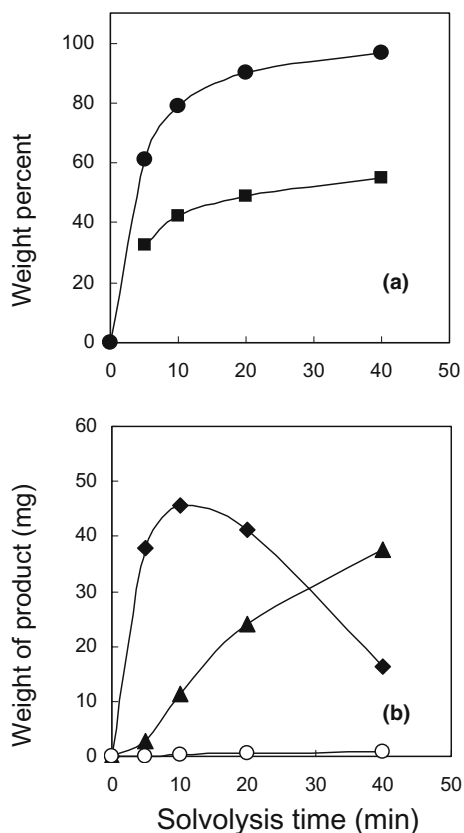


Fig. 5. **a** Solvolysis of wood using EC/ethylene glycol system and **b** chemical composition of the solvolyzed products with solvolysis time

Mechanism of cellulose solvolysis and the analysis method

We earlier 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; then the glucosides decomposed into a large quantity of levulinates.¹⁶ Even in the case of using EC, because EC decomposes into polyalcohols under acidic conditions, glucosides are produced at the early stage of the reaction, after which the glucosides decompose into a levulinic acid structure (Fig. 6).

As Bozzel et al.²⁴ noted, levulinic acid has attracted a great deal of attention as a building block for preparing useful chemical products. Fitzpatrick²⁵ and his company Biofine patented a way of producing levulinic acid in high yield in an acid-catalyzed hydrolysis reaction using two special continuous reactors in series (Biofine process). To produce levulinic acid in high yield, the reaction should form 5-hydroxymethyl furfural (HMF) derivatives as intermedi-

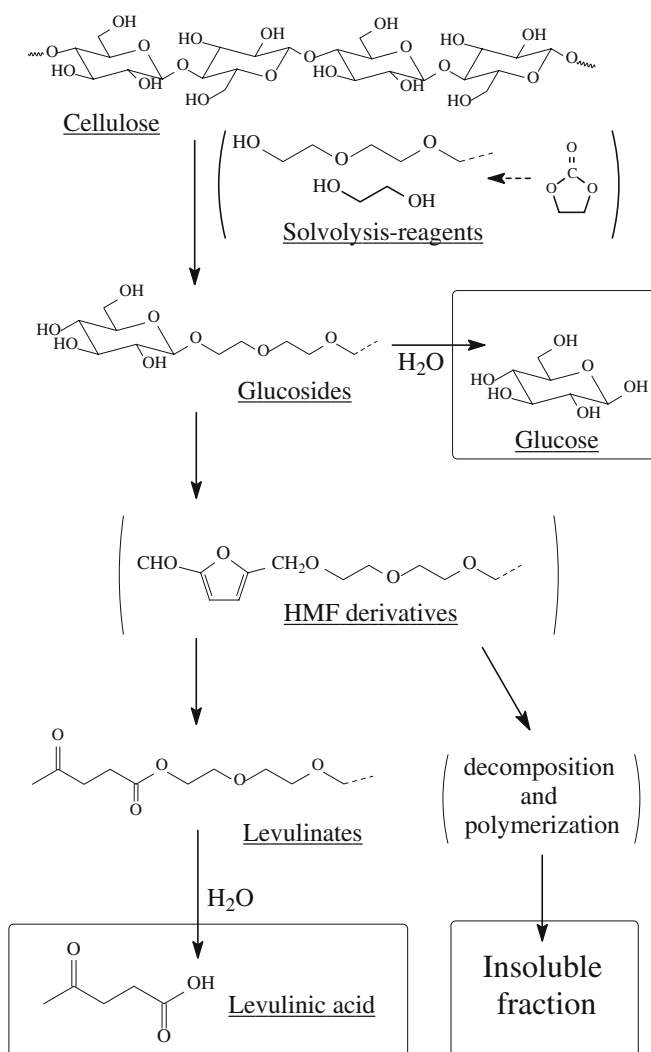


Fig. 6. Mechanism of cellulose degradation and decomposition during the solvolysis reaction, and the solvolyzed product analysis

ates. Horvat et al.²⁶ studied hydrolysis mechanisms of sugars and reported that the addition of water to the C2 and C3 positions of HMF would decompose HMF to produce levulinic acid. However, when water is added to the C4 and C5 positions, HMF decomposes into another structure leading to a condensed polymer. In the case of the solvolysis reaction, the HMF derivatives could be decomposed and polymerized to form insoluble residues.²³ In any case, to obtain a large quantity of levulinic acid, it will be important to control the reaction of HMF derivatives. Our study on high-yield levulinic acid production in an acid-catalyzed solvolysis reaction is in progress.

This article describes a method for analyzing the degraded cellulose in the solvolyzed products. Glucose content was measured by hydrolysis treatment of the water layer, and was defined as the glucoside content of the solvolyzed products. Additionally, levulinic acid content was measured by hydrolysis treatment of the chloroform layer and was defined as the levulinate content of the solvolyzed product (Fig. 6). The reaction conditions for the hydrolysis were optimized to give the highest yield of hydrolysis product. Because the composition of the poly (ethylene oxide) side of the glucosides and the levulinates vary with the reaction conditions of solvolysis, the method of applying the hydrolysis treatment after the fractionation will be the only way to analyze the glucose and levulinic acid content in the solvolyzed product.

In the case of the solvolysis of cellulose, a water-insoluble fraction might have been derived from condensed HMF derivatives.²³ As we have shown in this article, the water-insoluble fraction contains a levulinic acid structure that might be bonded to the condensed product. Although the amount of levulinic acid in this fraction was not high, this treatment is important to obtain the total conversion of levulinic acid.

Conclusions

Chemical analysis methods were used to determine the chemical composition of solvolyzed wood by focusing on the degraded products derived from cellulose. High boiling point reagents such as EC and PEG were used as solvolysis reagents and the reaction was carried out under atmospheric pressure. The solvolyzed product was separated into a chloroform layer, a water layer, and water-insoluble fraction. With the possibility of the chemical components in the solvolyzed product bonding to PEGs, which could lead to poor separability, the hydrolysis treatments were carried out before the HPLC analysis to determine the glucose content in the water layer and the levulinic acid content in the chloroform layer. The weight of the water-insoluble fraction and the amount of the bonded levulinic acid content in the water-insoluble fraction were also measured. The data clearly showed that all of the solvolysis reactions had the mechanism of cellulose degradation to produce glucosides, and the production of levulinates from the glucosides. The amount and the speed of the formation of glucosides

and levulinates depended on the conditions of the solvolysis.

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