Grafting of Ethylene Glycol Chains in Lignin during the Solvolysis for Biomass Conversion Using Ethylene Carbonate/Ethylene Glycol System

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(Received November 29, 2006; CL-061408; E-mail: kubos@ffpri.affrc.go.jp)

Solvolysis using mixed solvent of ethylene carbonate (EC) and ethylene glycol (EG) was applied to softwood. In this solvolysis, EG was substituted for hydroxy groups in the lignin molecules. Chain extension reaction of substituted EG occurred during the solvolysis, and DP = 3.0 of oligo EG chains are grafted by 60-min reaction. Linear EG chains are introduced into lignin molecules during the biomass conversion process without additional chemical modification.

There is an increasing interest in utilizing biomass as an alternative to current petrochemical based systems. For instance, the biomass conversion of forest biomass to produce bio-ethanol is receiving a lot of attention. Acid hydrolysis is often examined to convert cellulose component into glucose in that system. However, other components, such as lignin, are expected to be used only as a solid fuel due to its unattractive properties for commercial use. Additional chemical modification will be required to utilize acid hydrolyzed lignin.[1] If valuable lignin can be produced by one-step process, the process becomes more economically viable.

From our recent study, the novel biomass conversion using solvolysis reaction has been proposed. By using EC, which has high relative dielectric constant, as the reaction medium with small amount of mineral acid, cellulose is decomposed into formic and levulinic acid by one-step process in a short reaction period.[2] Levulinic acid is identified by US Department of Energy as one of the top-12 pivotal chemicals that should be derived from biomass in the future biorefinery.[3] Wide variety of products, such as herbicides, plastics, and fuel additives, can be derived from levulinic acid. Levulinic acid is currently examined to be produced by two-step acid hydrolysis under high pressure. One of the advantages of the solvolysis over the acid hydrolysis is that the conversion can be performed under atmospheric pressure. And, another advantage is that the lignin is recovered as a soluble material in this system. Moreover, depending on the solvolysis conditions, it is possible to produce thermally moldable lignin. This solvolysis is a potential method to produce an exploitable lignin as well as valuable chemicals from forest biomass by one-step process. In this paper, structural changes of lignin in this system are discussed to reveal the solvolysis reaction.

Wood meal of Japanese cedar (100–200 mesh) was mechanically stirred in quintuple weight of mixed solvent of EC and EG (mixed ratio is 8 to 2 by weight). H_2SO_4 (5% of the mixed solvent) was added in this suspension, and then heated at 150 °C. After a certain period, the reaction flask was quenched, and H_2SO_4 was neutralized with 2 M NaOH. Wood meal was almost solubilized in the mixed solvent during this process. Reaction products were also dissoluble in various organic solvents. As shown in Figure 1, insoluble fractions in dioxane/water, one of the good solvent for lignin, rapidly decreased in 20 min, and then kept constant at very low level (less than 2%) (Figure 1). Wood meal was solubilized with high reaction rate by the use of EC/EG. Low-molecular-weight products derived from cellulose, such as levulinic acid, hydroxymethylfurfural, and formic acid, were extracted from the reaction product with water, and high-molecular-weight products related to lignin were recovered as water insoluble solid (LF; lignin fractions). The yield of LF was over 60% (Figure 1), which was much higher than lignin content in original wood sample (35.2% as Klason lignin). There were no traces of carbohydrates detected by the ^{1}H NMR analysis of LF (data not shown).

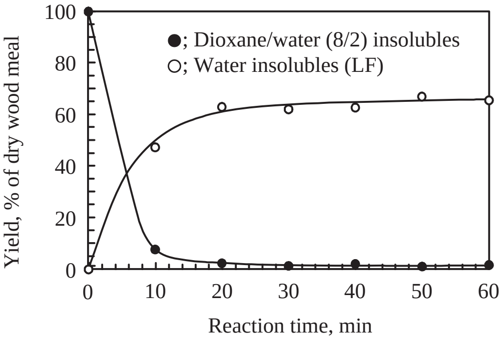

Figure 1. Yield of reaction residues and LF. Note that reaction residues are estimated as insoluble amount of reaction products with dioxane/water (8/2).

To examine the structural changes in lignin during this solvolysis, quantitative ^{13}C NMR analysis of LF was performed using chromium acetylacetonate as a relaxation reagent.[4] The resolution of quantitative ^{13}C NMR spectrum shown in Figure 2 was not enough to discuss the detailed structure of LF except for the signals appeared in the range from 75 to 55 ppm. However, the profile of this spectrum was comparable with a general spectrum for other lignin preparations. In the low magnetic field, a broad signal was appeared at the range from 175 to 170 ppm, which would be assigned to carbonyl carbons. It is well known that the carbonyl structures (Hibberts ketones) are introduced into lignin during the acidolysis through cleavage of the *β-O-4* linkage.[5] Introduction of certain amount of carbonyl groups were also indicated in FTIR analysis (see Supporting Information).[11] The characteristic clear signals found in the range from 75 to 55 ppm indicated the introduction of unusual sub-structures into LF. In a wood pulping using organic solvents such as ethanol and

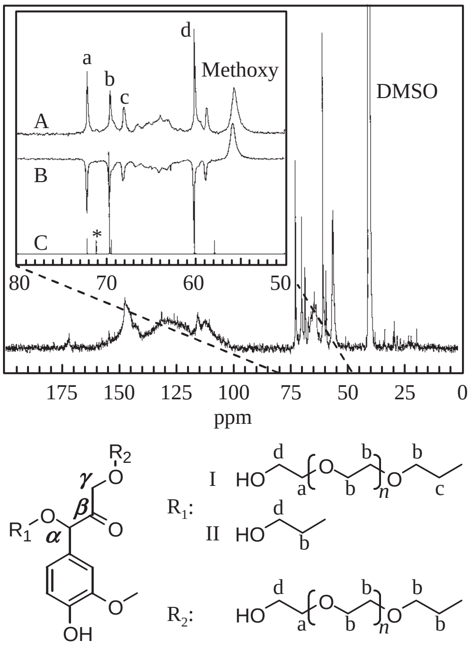

Figure 2. Quantitative ^{13}C NMR and DEPT spectra of LF recovered by 10 min solvolysis. A; Quantitative ^{13}C NMR, B; DEPT 135°, C; Quantitative ^{13}C NMR spectrum of monomethyl PEG.

1,3-butanediol, it is known that the solvents are nucleophilically substituted for hydroxy groups on α (benzyl) and γ positions of lignin sidechains.[6] EC undergoes decomposition into EG and carbon dioxide under the acidic conditions. EG would also be substituted for hydroxy groups in LF during the decomposition of EC. DEPT spectrum showed that all sharp signals appeared in this region was a methylene carbon except for the methoxy carbon (58.8 ppm) (Figure 2B). And, signals a, b, and d well corresponded to those of mono-methylated PEG (signal positions a, b, and d are 72.1, 69.6, and 60.1 ppm, respectively). Therefore, these signals could be assigned to the carbon in substituted EG chains. Signal c appeared at 68.1 ppm was assigned to the carbon connected to an oxygen atom on α position.[7] Assignment of these carbons in the substituted EG chains were shown in Figure 2 with the model structure of lignin unit.

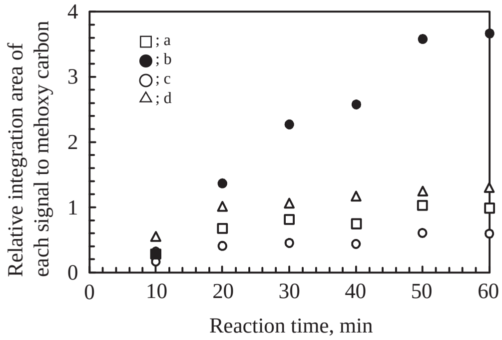

Figure 3. Relative integration area of each signal appeared on ^{13}C NMR spectrum shown in Figure 2.

The relative integration areas of all signals to that of a methoxy carbon increased with extended reaction period (Figure 3). This result indicates that the total amount of an introduced EG structure increased with extended reaction period. Signals a, c, and d slightly increased after 20 min. They were assigned to the carbons in the terminal end of EG chains. Therefore, the substitution reaction of EG onto α and γ positions in LF will almost come to equilibrium in 20 min. Total substitution of the EG chains was estimated to be 1.3 per methoxy group by 60 min solvolysis from the relative integration area of signal d. In contrast, signal b that was mainly assigned to a central units of EG chains increased over the whole experimental period up to 60 min, which suggested that the chain extension reaction of EG occurred continuously in this solvolysis. The substitution number of specific EG chains by the 60 min solvolysis can be estimated from Figure 3 as follows; The relative amount of the oligo EG chains substituted on α position (R_1: I) was approximately 0.62 from the relative integration area of signal c. The relative amount of the oligo EG chains on γ position (R_2) and a mono EG on α position (R_1: II) were calculated as 0.37 and 0.31 by subtracting c from a, and a from d, respectively. Assuming that the EG chain lengths on α and γ positions were equal, average DP was calculated as approximately 3.0.

Linear EG chains are successfully introduced into lignin molecules during the separation process. There are some methods reported for grafting linear alkyl- and oxyalkyl-chains on lignin to improve its plasticity[8] and solubility. The good solubility of LF with various solvents will be brought about by grafting of the amphiphilic EG chains. LF is likely to be utilized as an amphiphilic polymer[9] and/or functional gels,[10] although further improvement will be required to control the amount and length of EG chains introduced into LF.

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Published on the web (Advance View) March 3, 2007; doi:10.1246/cl.2007.502