Alkaline Polyethylene Glycol Treatment for Material Utilization of Lignin

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Kukjin YOON

Alkaline Polyethylene Glycol Treatment for Material Utilization of Lignin

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Kukjin YOON

Contents

Page

Chapter 1 Introduction 1
1 Background 1
2 Biorefinery 2
3 Lignin 7
4 Material utilization of lignin 18
5 Alkaline polyethylene glycol (PEG) treatment 23
6 Objective 23

Chapter 2 Preparation and composition of black liquor powder 24
1 Introduction 24
2 Experimental procedures 24
  2-1 Materials 24
    2-1-1 Black liquor powder 24
  2-2 Methods 25
    2-2-1 Preparation of purified lignin 25
    2-2-2 Determination of Klason method 25
    2-2-3 Evaluation of lignin content by UV method 26
    2-2-4 Chemical analysis of black liquor powder 27
3 Results and discussion 27
  3-1 Total lignin content of raw material 27
  3-2 Absorption coefficient of soda lignin for evaluation of UV method ... 27
  3-3 Composition of black liquor powder 28
4 Conclusion 33

CHAPTER 3 Preparation and characterization of alkaline PEG-treated lignin from black liquor powder 34
1 Introduction 34
2 Experimental procedures 36
  2-1 Materials 36
    2-1-1 Black liquor powder 36
  2-2 Methods 37
    2-2-1 Alkaline PEG treatment 37
    2-2-2 Evaluation of lignin content 37
    2-2-3 Thermal melting characteristics 37
    2-2-4 Nuclear magnetic resonance (NMR) analysis 38
3 Results and discussion 38
  3-1 Thermal melting characteristics of the alkaline PEG-treated lignin 38
  3-2 Effect of the reaction temperature of alkaline PEG treatment on

grafting PEG onto lignin 45
3-3 Reaction mechanism of the alkaline PEG treatment of lignin 47
4 Conclusion 51

Chapter 4 Preparation and characterization of alkaline PEG-treated lignin from purified and acid-soluble lignin (Model experiment) 52
1 Introduction 52
2 Experimental procedures 54
2-1 Materials 54
2-1-1 Black liquor powder 54
2-1-2 Purified lignin 55
2-1-3 Acid-soluble lignin fraction 55
2-2 Methods 56
2-2-1 Alkaline PEG treatment of black liquor powder 56
2-2-2 Alkaline PEG treatment of the purified lignin 56
2-2-3 Evaluation of lignin content 57
2-2-4 Thermal melting characteristics 58
2-2-5 Thermomechanical analysis (TMA) 58
2-2-6 Nuclear magnetic resonance (NMR) analysis 58
3 Results and dicussion 59
3-1 Effect of the PEG molecular weight 59
3-2 Thermal melting characteristics of alkaline PEG-treated lignin 61
3-3 Chemical structure of alkaline PEG-treated lignin 72
3-4 Effect of the reaction time of alkaline PEG treatment on grafting PEG onto lignin 77
3-5 Reaction of acid-soluble lignin 83
4 Conclusion 89

Chapter 5 General conclusions 90

References 93

Acknowledgements 99

List of figures

Figure 1. Biorefinery concept (Ragauskas *et al.*, 2006; Holladay *et al.* 2007) 5

Figure 2. A 3-platform (C5 and C6 sugars, electricity and heat, and lignin) biorefinery using wood chips for the production of bioethanol, electricity, heat, and phenols (Jungmeier 2014) 6

Figure 3. Average chemical composition of pine (*Pinus sylvestris*) and birch (*Betula pendula*) (% of the wood dry solids) (Alén 2000) 12

Figure 4. The structures of three C_6C_3 precursors of lignins: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) structure 13

Figure 5. Lignin structure of a simulated softwood (spruce) lignin by Adler (1977) 14

Figure 6. Four types of radical resonance from coniferyl alcohol (Higuchi 1982; Fukushima 2010) 15

Figure 7. Main structures and frequencies of the inter-unitary linkages in native softwood and hardwood lignins (Higuchi 1982; Alén 2000; Yamauchi and Saka 2013) 17

Figure 8. Potential utilizations of lignin (Holladay *et al.* 2007; Higsson 2011; Gosselink 2011) 20

Figure 9. Depiction of low-cost carbon fiber production from lignin (Kline and Companies program 2004; Holladay *et al.* 2007) 21

Figure 10. Phenol derivatives that canbe produced using current technology

(Holladay *et al.* 2007) 22
Figure 11. Absorption (ABS) coefficient of soda lignin as determined by UV spectroscopy 30
Figure 12. Determination of the alkali content of dried black liquor powder by hydrochloric acid titration 31
Figure 13. Thermal softening behavior of the alkaline PEG-treated lignin with elevating temperature to determine softening point (a) PEG 2000 treated and (b) PEG 1000 treated at 120 °C 41
Figure 14. Thermal softening length of the alkaline PEG-treated lignins (Treatment temperature at 120 °C: (a) PEG 2000 and (b) PEG 1000).... 42
Figure 15. Thermal softening length of the alkaline PEG-treated lignins (Treatment temperature at 160 °C: (a) PEG 400 and (b) PEG 1000)...... 44
Figure 16. Effect of the PEG molecular weight on the lignin content of the alkaline PEG-treated lignin at 120 °C(●) and 160 °C(■) 46
Figure 17. ^{13}C－NMR spectrum of alkaline PEG-treated lignin prepared from black liquor powder with PEG 400 49
Figure 18. A reaction mechanism between soda lignin and PEG in the alkaline PEG treatment 50
Figure 19. Effect of PEG molecular weight on the lignin content of alkaline PEG-treated lignin prepared from purified lignin 60
Figure 20. Thermal softening behavior of alkaline PEG-treated lignin

prepared from purified lignin with increasing temperature to determine softening point 64

Figure 21. Thermal softening behavior of alkaline PEG-treated lignin prepared from black liquor powder with increasing temperature to determine softening point 65

Figure 22. Thermal softening length of alkaline PEG-treated lignin prepared from black liquor powder 66

Figure 23. Thermal softening length of alkaline PEG-treated lignin prepared from purified lignin 67

Figure 24. Thermal mechanical analysis of purified lignin 69

Figure 25. Thermal mechanical analysis of alkaline PEG-treated lignin prepared from black liquor powder 70

Figure 26. Thermal mechanical analysis of alkaline PEG-treated lignin prepared from purified lignin 71

Figure 27. ^{13}C-NMR spectrum of purified lignin 74

Figure 28. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 200 75

Figure 29. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 400 76

Figure 30. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 1000 77

Figure 31. A reaction mechanism of alkaline PEG treatment 80

Figure 32. Effect of the reaction time on the lignin content of the alkaline PEG-treated lignin prepared from purified lignin 81

Figure 33. ^{13}C—NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin (Reaction time : 60 min) 82

Figure 34. Percentage of acid-soluble and acid-insoluble lignin in black liquor powder 85

Figure 35. Preparation scheme for acid-soluble lignin of black liquor powder 86

Figure 36. ^{13}C—NMR spectrum of alkaline PEG-treated lignin prepared from acid-soluble lignin fraction using EG 87

Figure 37. ^{13}C—NMR spectrum of alkaline PEG-treated lignin prepared from acid-soluble lignin fraction using PEG 1000 88

List of tables

Table 1. Functional groups of native lignin (per 100 C_6C_3 units) (Alén 2000) 16

Table 2. Total lignin contents of dried black liquor powder and purified lignin 29

Table 3. Composition of black liquor powder 32

Table 4. Thermal melting characteristics of the alkaline PEG-treated lignins 43

Table 5. Thermal melting characteristics of alkaline PEG-treated lignin prepared from black liquor powder and purified lignin 68

Abbreviation

- ABS: Absorption
- AQ: Anthraquinone
- CF: Carbon fiber
- DEG: Diethylene glycol
- EG: Ethylene glycol
- NMR: Nuclear magnetic resonance
- PEG: Polyethylene glycol
- SEC: Size exclusion chromatography
- T_g: Glass transition temperature
- T_s: Thermal softening temperature
- TMA: Thermal mechanical analysis
- UV: Ultra violet

Chapter 1 Introduction

1 Background

Lignin is one of the most abundant biomacromolecules on Earth. The recent focus on sustainable materials has promoted interest in lignin as a source of fuel and new materials. Lignin prepared through industrial pulping (cooking) processes is called technical lignin. Chemical pulping accounts for 70% of the total worldwide production of lignin (Alén 2000). The great majority of chemical pulps of lignin are obtained by alkaline cooking. Generally, the sulfate or kraft process and the soda process are the two principal alkaline cooking techniques. Sodium hydroxide is the principal cooking chemical in both processes, while sodium sulfide is an additional active pulping component in kraft cooking. Alkaline solution (white liquor) is added to wood chips at high temperature and pressure, and cellulose is produced from the wood by dissolving almost all of the lignin and a large portion of the hemicelluloses into the spent liquor (black liquor). The main object of the cooking processes for delignification is to facilitate the disintegration of wood into its fibrous components.

The present and future utilization of lignin is an extensive and increasingly important field of study (Fengel and Wegener 1983). One reason for this can be seen in the increasing appreciation of renewable raw materials. Lignin as a raw material is still far from being utilized intensively. This is true in spite of its large potential for multiple purposes due to its chemistry, properties, and the huge amounts of it produced worldwide by pulping processes. However, at the present time, lignin is mainly used as an energy source. Most technical lignin is used for energy purposes because the recovery of the chemicals used in pulping processes is based on the incineration of the black liquor. The calorific value of the organic material in the black liquor is an important economic factor, especially when considering the high prices of gas and oil, though kraft lignin can also be used for high-value non-fuel purposes (Barton 1978; Zhu and Theliander 2015). New fields of lignin utilization as a starting material would be opened up by the development of processed lignins with improved properties.

2 Biorefinery

In modern times, the global population has been consuming many commodity products such as energy, materials, plastics, and transportation fuels. These commodity products almost all originate from fossil resources, which are non-renewable resources and contribute to CO_2 emissions. Therefore, alternatives should be sought with low carbon emissions. Currently available alternatives include renewable resources such as wind, solar energy, and biomass. Biomass represents an abundant renewable resource for the production of bioenergy and biomaterials.

Shifting society’s dependence away from fossil resources to renewable biomass resources is generally viewed as an important contributor to the development of a sustainable industrial society and the effective management of CO_2 (Ragauskas *et al.* 2006). It is thought that this shift will need research and development to increase the efficiency and sustainablility of biorefinery facilities. The term “biorefinery” encompasses the technologies and industries related to the production of bio-fuels and chemicals using biomass as a raw material. Biorefineries input biomass as a carbon source and can generate fuel, power, and products as outputs (Figure 1) (Ragauskas *et al.*, 2006; Holladay *et al.* 2007). It is widely believed that the next generational change in the use of bioresources will come from a total integration of the use of innovative plant resources, synthesis of biomaterials, and generation of bio-fuels and biopower.

Wood is the world's largest source of biomass. Woody biomass offers many possibilities as a raw material not only for the energy sector but also for the chemical industry due to its chemical composition, abundant availability, and relatively low costs when its conversion to products can be carried out in an economic and sustainable manner (Gosselink, 2011). The abundant availability of woody biomass is supported by the large worldwide annual woody biomass production of about 200 billion (200×10^9) tons per year (Zhang 2008), compared to the 0.25–0.3 billion tons ($0.25–0.3 \times 10^9$) tons per year of organic chemicals produced by the chemical industry (Haveren *et al.* 2008).

Woody biomass is mainly composed of cellulose, hemicellulose, and lignin. About 95% of synthetic polymers (plastics, synthetic fibers, and synthetic rubbers) could be derived from woody materials, although the circuitous synthesis route required for some of them might make such processes uneconomic at this time (Goldstein, 1975). The key to the most efficient use of biomass is to design a suitable and sustainable integral biorefinery to separate biomass into its major compounds and generate the highest value-added products from all fractions. In Figure 2, an example is given of a 3-platform (C5 & C6 sugars, electricity & heat, and lignin) biorefinery that uses wood chips to produce bioethanol, electricity, heat, and phenols (Jungmeier 2014). The ideal biorefinery would contribute to sustainability not only through its inherent dependence on sustainable bioresources, but also by recycling waste, with the entire process being carbon neutral (Ragauskas *et al.* 2006).

In the second generation production process for bioethanol, woody biomass is separated into pulp (cellulose fiber). The production of bioethanol from woody biomass has been proposed as a strategy to alleviate the pressure on global fossil fueal reserves that are forecast to eventually become insufficient to meet worldwide demand (Chum *et al.* 1985). This biorefinery technology has the potential to generate sulfur-free lignin in black liquor. Sulfur-free lignin can be obtained by soda cooking and is an emerging class of lignin product (Lora 2002; Lora and Glasser 2002). The recovery of sulfur-free lignin in the black liquor is based on precipitation, followed by liquid/solid separation and drying.

Several technologies have been under development for wood biorefineries in which the lignin fraction is mainly considered as an energy source. Lignin also has a high potential for utilization as a material in the construction and textile industries. This will be described again in detail in section 4 “Material utilization of lignin” of this chapter.

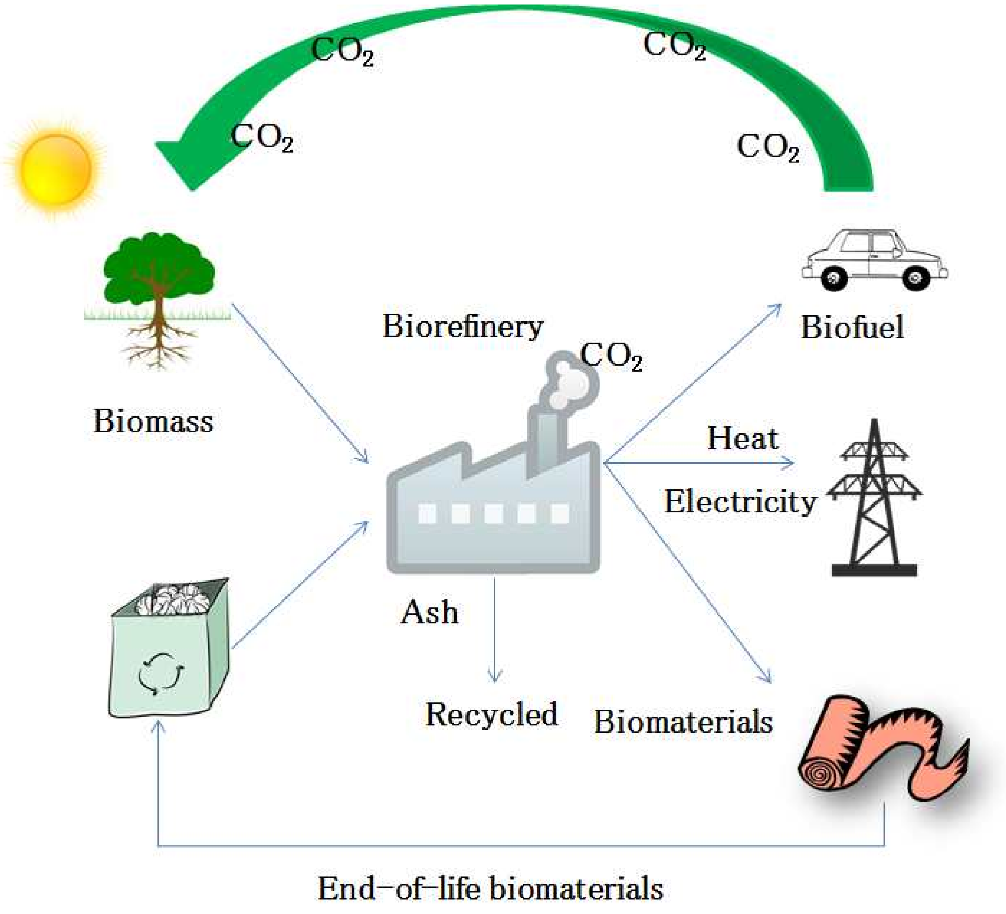


Figure 1. Biorefinery concept (Ragauskas *et al.*, 2006; Holladay *et al.* 2007)

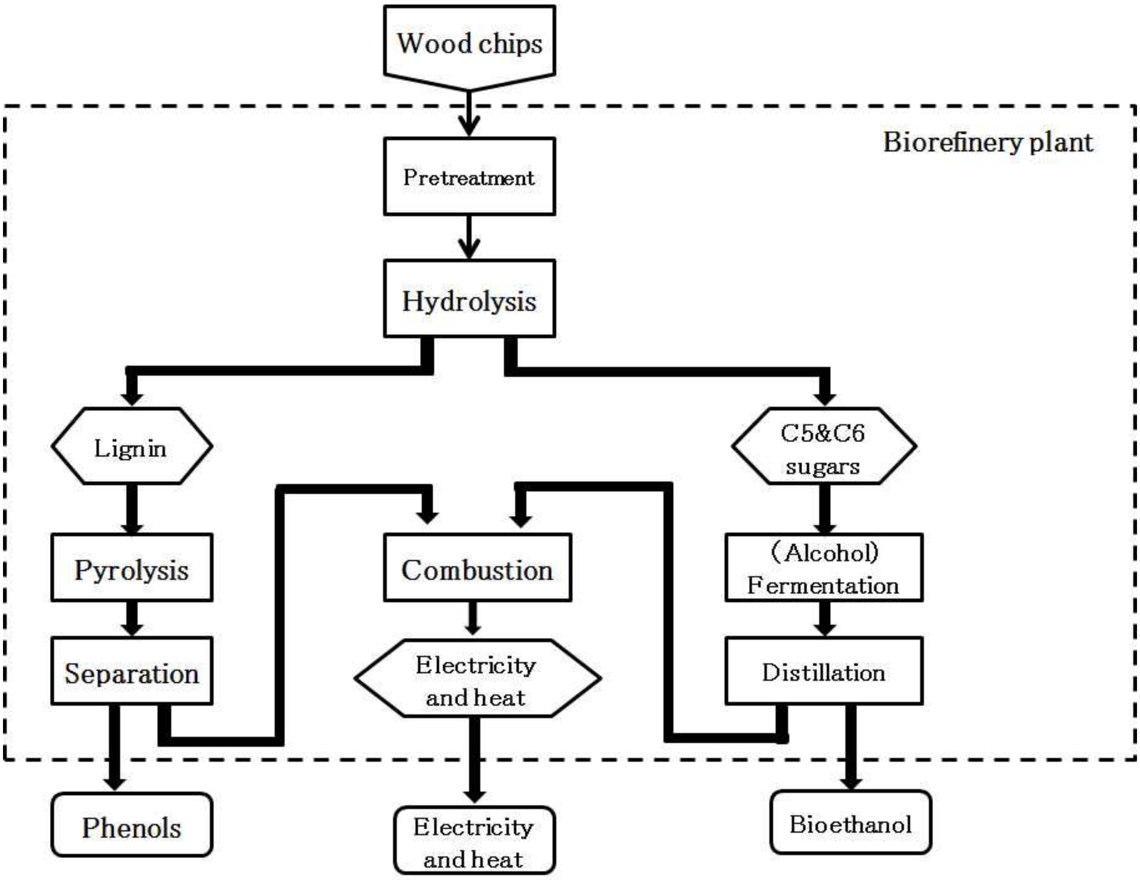


Figure 2. A 3-platform (C5 and C6 sugars, electricity and heat, and lignin) biorefinery using wood chips for the production of bioethanol, electricity, heat, and phenols (Jungmeier 2014)

3 Lignin

Lignin is one of the most abundant natural organic polymers on Earth and is found in all woods. It has a complex structure containing both aromatic and aliphatic molecules. The isolation of lignin from wood was first described in a report by the French scientist Payen in 1838, and it was given its current name in 1857 by Schulze. Lignin occurs widely in the middle lamellae and secondary cell walls of higher plants and plays a key role in structural tissues as a building material, where it confers strength, rigidity, and resistance to environmental stresses (Ralph *et al.* 2007). Wood consists of cellulose (40–45%), hemicellulose (25–35%), and lignin (20–30%) (Alén 2000). Softwoods and hardwoods typically differ from each other in their chemical compositions. Figure 3 illustrates the typical gross chemical compositions of a commercial softwood and a hardwood (Alén 2000). This figure summarizes the main differences between pine (*Pinus sylvestris*) and birch (*Betula pendula*).

Lignin is a hydrophobic material; therefore, it makes plant cell walls impermeable to water, and thus ensures the efficient transport of water and nutrients between the cells (Henriksson 2009; Norberg 2012). Lignin is also an amorphous polymer with a distinctly different chemical structure from that of the other macromolecular constituents of wood. In its native state, or as found in plants, lignin is referred to as protolignin. It is widely accepted that the biosynthesis of lignin stems from the polymerization of three types of phenylpropane units, which are also referred to as monolignols (Freudenberg and Neish 1968; Sarkanen and Ludwig 1971; Lewis 1999; Ralph *et al.* 1999). Lignin is produced by the enzymatic dehydrogenative polymerization of coniferyl alcohol, syringyl alcohol, and coumaryl alcohol (Figure 4). The proportions of these precursors in lignins vary depending on their botanical origin. Normal softwood lignins are usually referred to as having a guaiacyl (G) structure because the structural elements are derived principally from coniferyl alcohol (more than 90%), with the remainder consisting mainly of *p*-coumaryl alcohol. In contrast, hardwood lignins, generally termed as having a G-syringyl (S) structure, are mainly composed of coniferyl alcohol and sinapyl alcohol in varying ratios (about 50% of each alcohol). Grass lignins are also classified as having a G-S structure, although they additionally contain significant amounts of structural elements derived from *p*-coumaryl alcohol and some aromatic acid residues (about 40% coniferyl alcohol, about 40% sinapyl alcohol, and about 20% other precursors) (Alén 2000). The biosynthesis of lignins occurs via a process comprising various oxidative coupling reactions of the resonance-stabilized phenoxy radicals obtained from these α, β-unsaturated C_6C_3 alcohol precursors, leading to the formation of a randomly cross-linked macromolecule. Lignins are built in plants starting from the three basic monolignols via oxidative phenolic coupling reactions to generate the polymer, as shown in Figure 5 (Adler 1977). Lignin polymers are heterogeneous in terms of their molecular composition and the linkage types between the phenyl propane monomers and the S, G, and *p*-hydroxyphenyl (H) structures. These structures are derived from the monolignols sinapyl alcohol, coniferyl alcohol, and coumaryl alcohol, respectively (Figure 4). Figure 6 illustrates the dehydrogenation of coniferyl alcohol and the resonance-stabilized phenoxy radicals (Higuchi 1982; Fukushima 2010). The polymerization process is initiated by the oxidation of the monolignol phenolic hydroxyl groups. The oxidation reaction itself has been shown to be catalyzed via an enzymatic route. The enzymatic dehydrogenation is initiated by an electron transfer that yields reactive monolignol species and free radicals (Figure 6). Subsequent nucleophilic attack by water, alcohols, or phenolic hydroxyl groups on the benzyl carbon of the quinone methide intermediate will restore the aromaticity of the benzene ring. The generated dilignols will then undergo further polymerization (Chakar and Ragauskas 2004).

The lignin composition of plants differs not only between species, but also between different tissues of an individual plant variety. In softwood lignin, coniferyl alcohol is the predominant building unit (over 95% G structural elements), while in hardwoods the ratio between coniferyl and synapyl alcohols shows considerable variation (Henriksson 2009; Gosselink 2011). Lignin contains a range of chemical functional groups, which is partly the result of the extraction method. The main groups in protolignin (native lignin) are hydroxyl (aromatic and aliphatic), methoxyl, carbonyl, and carboxyl groups (Figure 5). The content of functional groups in lignin varies considerably among plant species and within individual cell walls, and therefore only approximate values for the frequencies of different functional groups can be given (Table 1) (Alén 2000). Depending on its precursors, the lignin polymer contains characteristics of methoxyl groups, phenolic hydroxyl groups, and some terminal aldehyde groups in the side chain.

The solubility of lignins is affected by the proportion of these functional groups. Most lignins are quite soluble in alkaline solutions due to the ionization of the hydroxyl and carboxyl functional groups. However, the exact structure of native lignin remains virtually unknown (Chakar and Ragauskas, 2004). The majority of chemical bonds in the native lignin polymeric network are the C-O-C ether linkage type between the phenyl propane structures, mainly β-O-4, while the residue consists of C-C bonds between these structures (Higuchi 1982; Yamauchi and Saka 2013). Figure 7 summarizes the dominant bond types and their frequencies. In addition, numerous miscellaneous linkages and minor structures are known (Higuchi 1982; Alén 2000; Yamauchi and Saka 2013). It is also evident that the frequency of these groups can vary according to the morphological location of lignin.

Almost all lignins extracted from woody materials by the chemical pulping industry are burned to generate energy and recover chemicals. During the chemical pulping process, roughly half of the wood substance, by volume, degrades and dissolves. The organic matter in the black liquor is composed of the degradation products of lignin and polysaccharides in addition to a minor fraction comprising extractives. The sulfate or kraft (kraft means strength or power in German and Swedish) process and the soda process are the two principal alkaline pulping techniques and the basis for several modified alkaline processes (Fengel and Wegener 1983). Sodium hydroxide is the principal cooking chemical in both processes, while in sulfate pulping, sodium sulfide is an additional active pulping component. The kraft process is not only the dominant alkaline pulping process for wood, but also the most important of all current industrial pulping processes. Kraft pulps are obtained in higher yields and with properties superior to those of soda pulps. The lignin obtained by the kraft process is partly cleaved and thiol groups (-SH) are introduced into the solubilized lignin. The purpose of kraft cooking is to obtain cellulose. On the other hand, a lignin obtained by the soda process is a sulfur-free lignin (soda lignin) (Lora and Glasser 2002; Ikeda and Magara 2015). Soda lignins with a moderate macromolecular size can be obtained. In this study, cooking of lignin was performed using soda-anthraquinone (AQ) cooking to obtain black liquor for preparing a starting material. After the soda-AQ cooking process, the black liquor was used in this study. The soda-AQ black liquor was spray-dried and vacuum-dried. The preparation of the spray-dried black liquor powder will be described fully in Chapter 2.

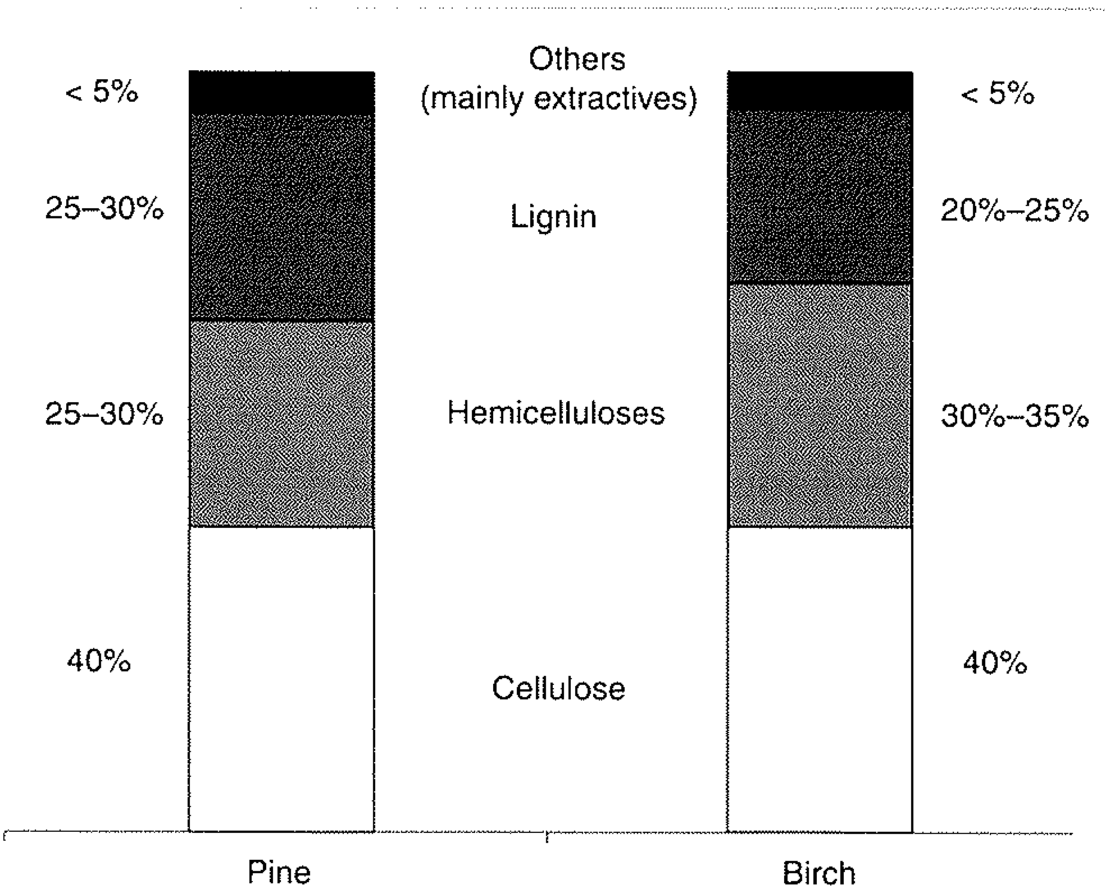


Figure 3. Average chemical composition of pine (*Pinus sylvestris*) and birch (*Betula pendula*) (% of the wood dry solids) (Alén 2000)

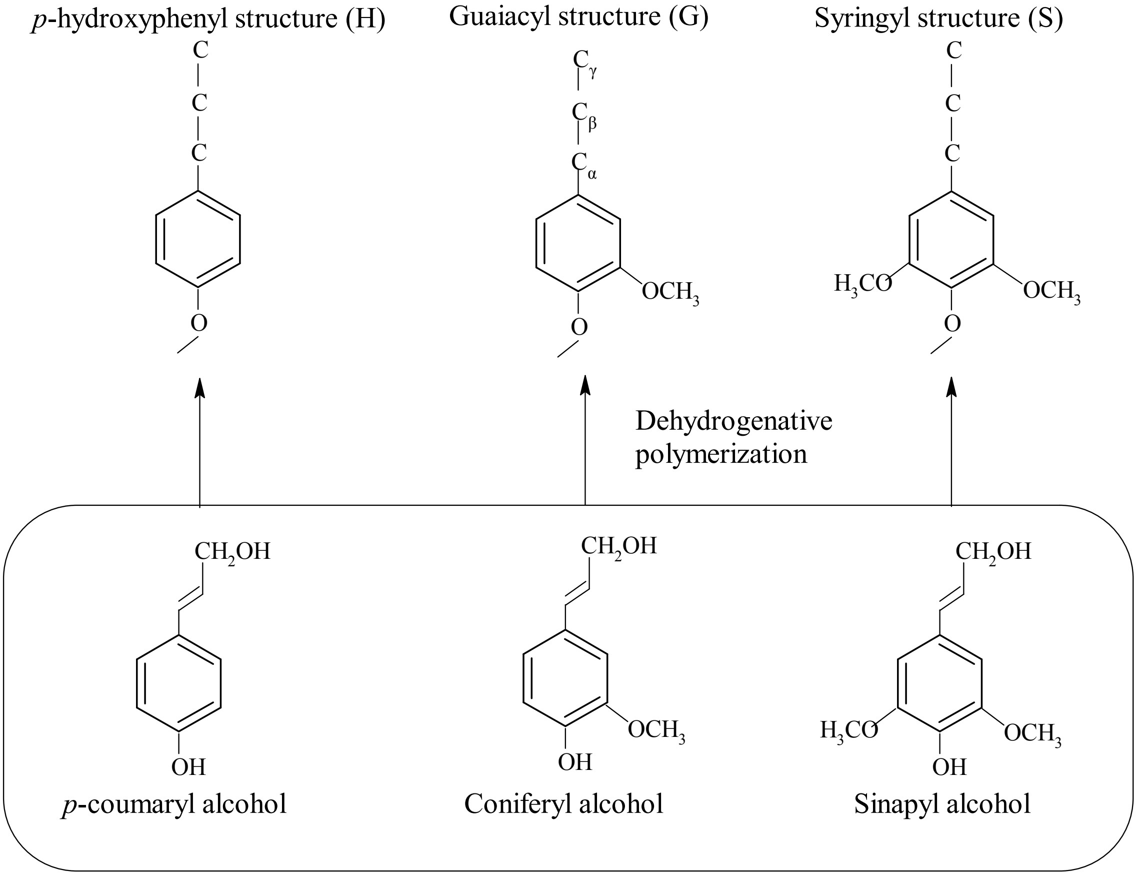


Figure 4. The structures of three C_6C_3 precursors of lignins: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) structure

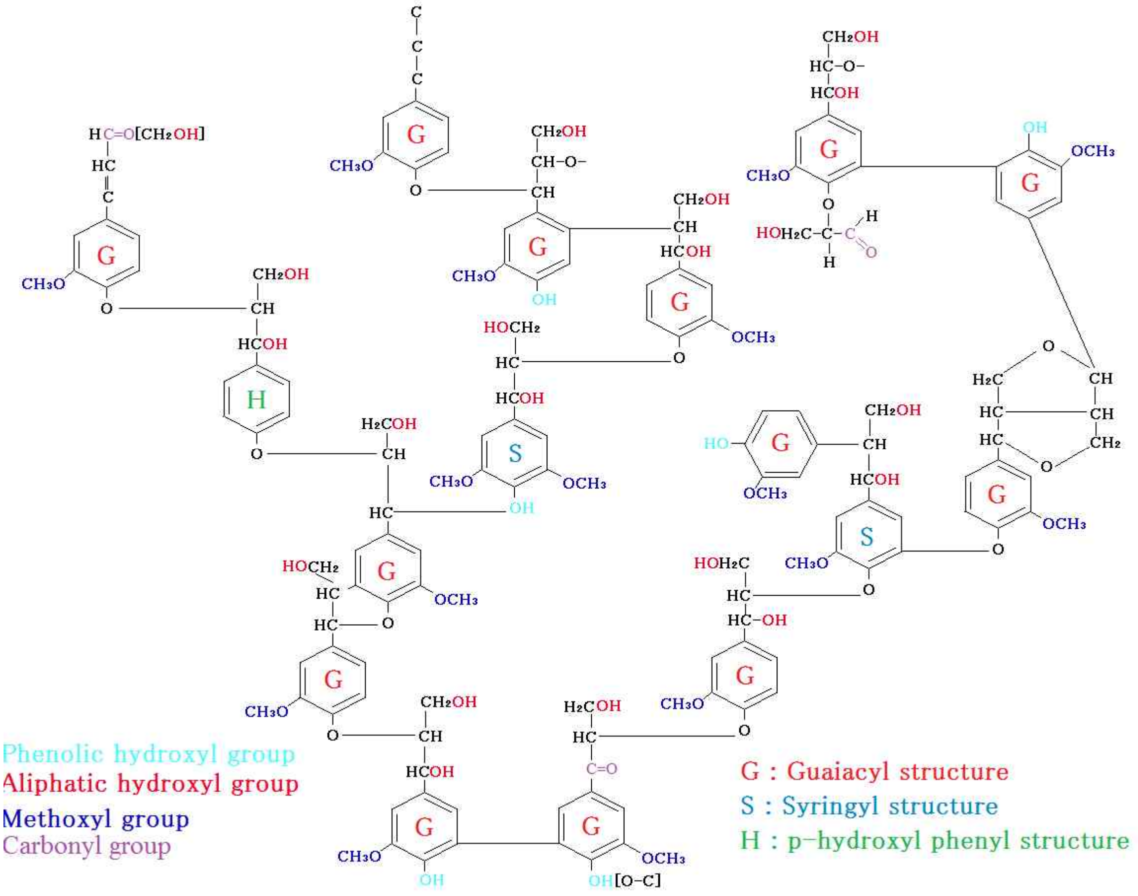


Figure 5. Lignin structure of a simulated softwood (spruce) lignin by Adler (1977)

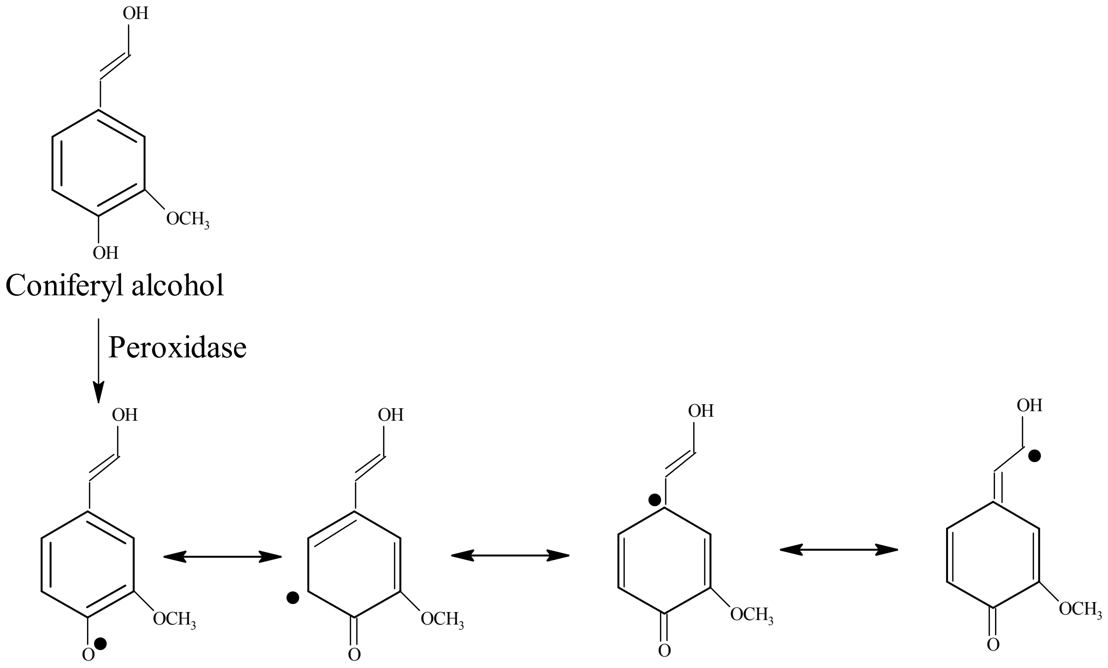


Figure 6. Four types of radical resonance from coniferyl alcohol (Higuchi 1982; Fukushima 2010)

Table 1. Functional groups of native lignin (per 100 C_6C_3 units) (Alén 2000)

Functional group	Softwood	Hardwood
Phenolic hydroxyl	20 - 30	10 - 20
Aliphatic hydroxyl[a]	115 - 120	110-115
Methoxyl	90 - 95	140 - 160
Carbonyl	20	15

[a] Total sum of the primary and secondary hydroxyl groups.

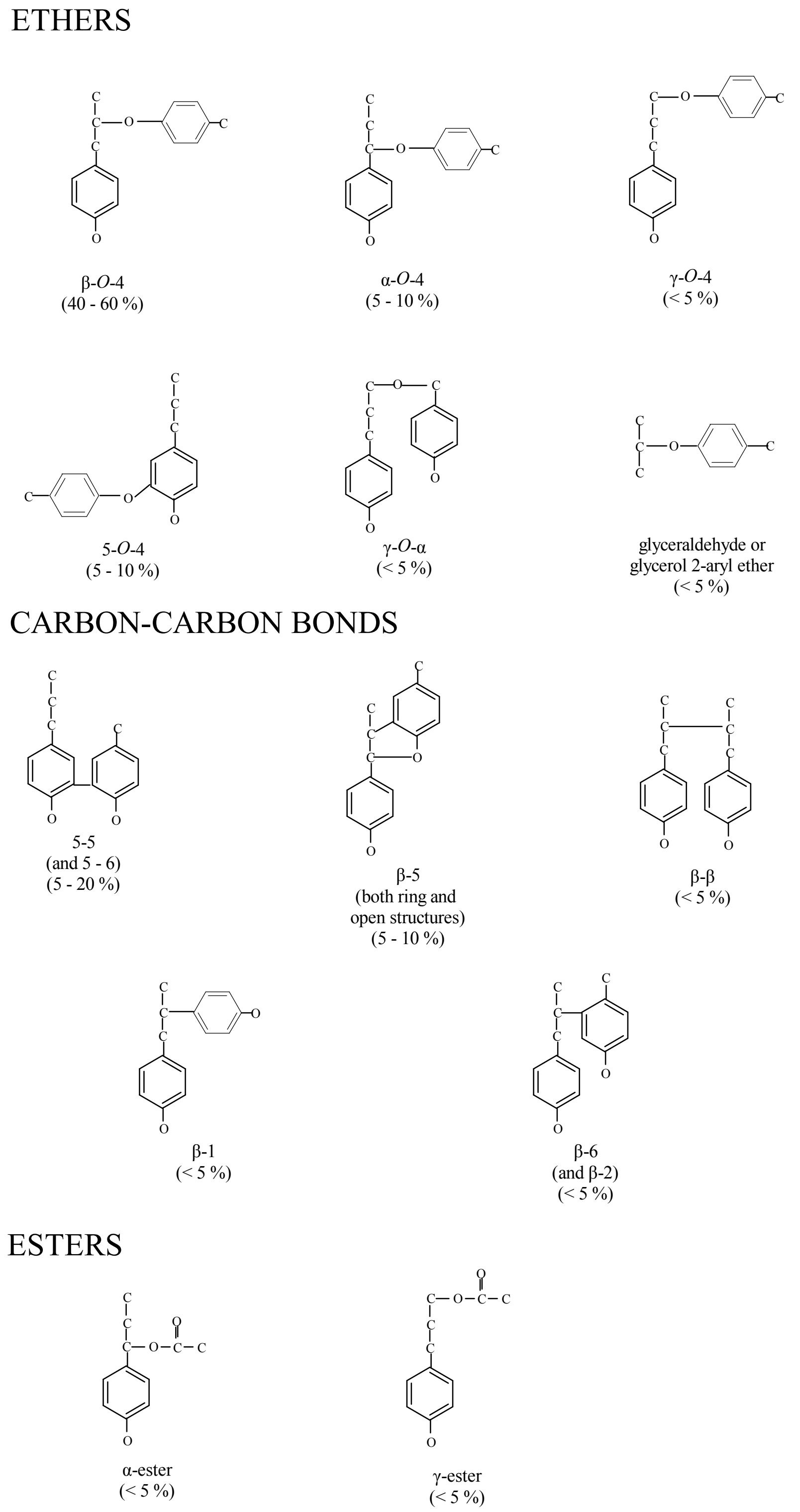


Figure 7. Main structures and frequencies of the inter-unitary linkages in native softwood and hardwood lignins (Higuchi 1982; Alén 2000; Yamauchi and Saka 2013)

4 Material utilization of lignin

Lignin is a versatile raw material with many potential utilizations (Lora and Glasser 2002; Stewart 2008; Doherty *et al.* 2011). The potential utilizations of lignin can readily be divided into three categories: 1. fuels; 2. macromolecules; and 3. aromatics and other chemicals. These categories can also be distinguished according to the time-to-market, with category 1 as current or near-term utilizations (immediate), category 2 as medium-term utilizations, and category 3 as longer-term utilizations (Holladay *et al.* 2007).

In the category of fuels, lignin is used as a carbon source for energy production by gasification. Macromolecules that could potentially be produced from lignin include dispersants, binders, and carbon fiber (CF). The production of aromatics involves the use of technologies to cleave the lignin structure into monomers without sacrificing the aromatic rings for the production of polymer building blocks, including the aromatic monomers benzene, toluene, xylene, phenol, and vanillin. A representative diagram of the various utilizations of lignin is shown in Figure 8 (Holladay *et al.* 2007; Higsson 2011; Gosselink 2011).

Due to its polyaromatic macromolecule property, lignin represents a potential low-cost source of carbon that may be suitable for displacing synthetic polymers such as polyacrylonitrile in the production of CF (Figure 9) (Kline and Co. 2004; Holladay et al. 2007). Using lignin-based CF improves raw material availability, decreases raw material sensitivity to the price of fossil oil, and decreases environmental impacts. The initial step in economical lignin-based CF manufacturing requires lignin to have a thermal melting property. The technical barriers in processing lignin to have this property include the development of a low-cost purification method to remove bound short polysaccharides, salts, particulate contaminants, water, and other volatiles. Another technical challenge is dealing with lignin molecular weight polydispersity. A final barrier is the development of practical new methods to process, stabilize, and derivatize lignin and thus optimize its thermal melting properties such as its melt-flow, glass transition temperature (T_g), and thermal softening temperature (T_s). Another goal is to make lignin from different sources acceptable as a raw material for high rate melt-spinning and simultaneously capable of delivering high carbon weight yields when the melt-spun lignin fiber is thermally converted to CF (Holladay *et al.* 2007; Norberg 2012; Jian 2013).

As above, some derivatized lignins for industrial utilization have focused on improvements in thermal property. It is well recognized that the thermal melting property generally follows T_g, with the thermal melting property increasing as T_g declines. Lignins with an appropriate thermal melting property may be useful as plasticizers. Some lignins, such as soda lignin, do not exhibit melt-flow with increasing temperature. Taken together, establishing processing techniques to control the thermal behavior of lignin is one of the most important challenges for improving its material utilization.

Phenol and some of its commercially important derivatives produced using current technology are shown in Figure 10 (Holladay *et al.* 2007). In 2009, phenol was utilized as feedstock to produce bisphenol-A (which is the end-product of 48% of phenol processed worldwide), phenol resin (25%), caprolactam (11%), alkyl phenols (4%), xylenols (4%), aniline (2%), and others (Sadhukhan *et al.* 2014).

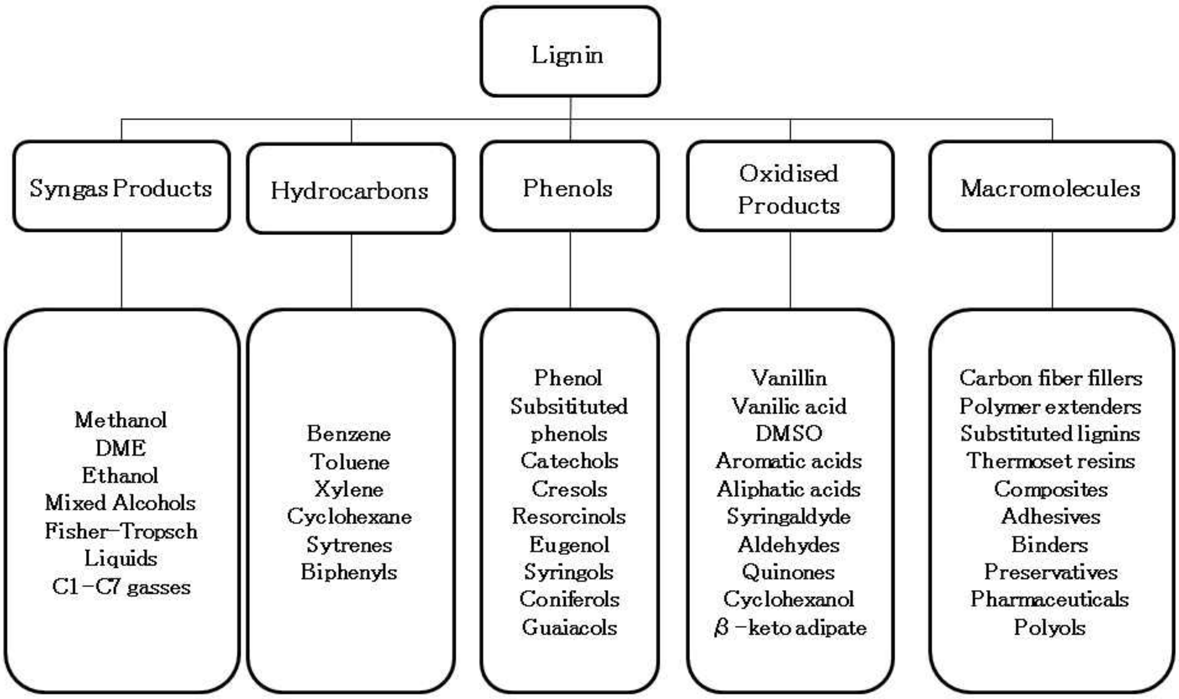


Figure 8. Potential utilizations of lignin (Holladay *et al.* 2007; Higsson 2011; Gosselink 2011)

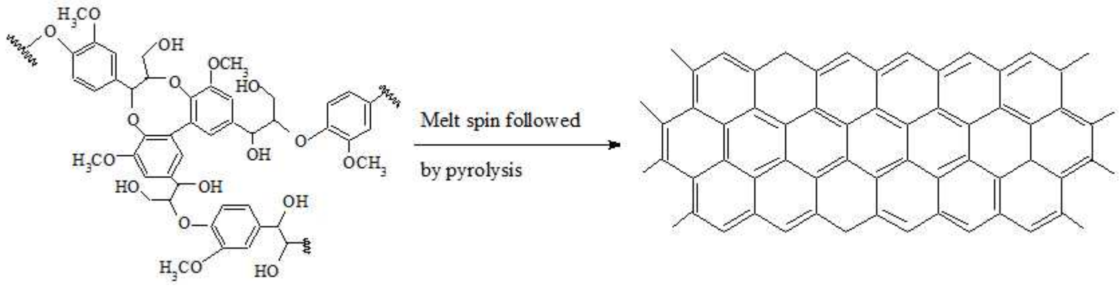


Figure 9. Depiction of low-cost carbon fiber production from lignin (Kline and Companies program 2004; Holladay *et al.* 2007)

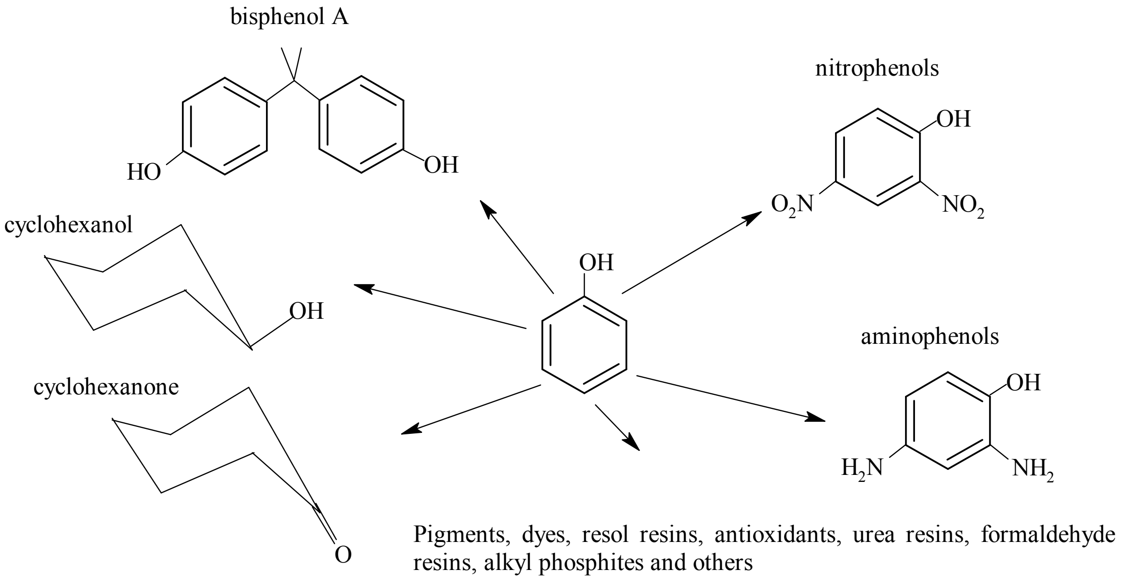


Figure 10. Phenol derivatives that canbe produced using current technology (Holladay *et al.* 2007)

5 Alkaline polyethylene glycol (PEG) treatment

Alkaline PEG treatment is a new method for improving the material utilization of lignin. In the experiments for this thesis, I performed alkaline PEG treatment using black liquor powder produced by softwood soda-AQ cooking. In the process, the black liquor powder was directly treated with PEG under alkaline conditions to produce a thermal melting material. This lignin modification method is termed alkaline PEG treatment.

6 Objective

The aim of this thesis was to investigate the possibility of using softwood soda-AQ lignin as a commercial material. First, a process for the preparation of black liquor powder from black liquor was described (Chapter 2). Then, the chemical and thermal properties of alkaline PEG-treated lignin prepared from black liquor powder were studied (Chapter 3). To clarify the reaction of softwood soda-AQ lignin in the alkaline PEG treatment, experimental alkaline PEG treatments were performed using purified acid-soluble lignin (Chapter 4).

Chapter 2 Preparation and composition of black liquor powder

1 Introduction

Lignins in wood are removed by alkaline cooking procedures such as the soda and kraft processes. In the plant cell wall, lignin is closely associated with polysaccharide structures including cellulose and hemicellulose. Woody materials are used as a base material for the extraction of cellulosic fibers to manufacture paper. During the production of paper, lignin is chemically degraded under alkaline conditions. The majority of the degraded lignin is contained in spent liquor, which is called black liquor. The black liquor containing the lignin fraction is mostly used as fuel feedstock for industrial plant operation. Spray drying is a method of producing a dried powder from a liquid by rapidly drying it under hot air. Lignin in the black liquor powder would be modified by alkaline PEG treatment. First, it is necessary to clarify the preparation and composition of the raw materials used this study.

2 Experimental procedures

2-1 Materials

2-1-1 Black liquor powder

Black liquor was obtained from the bioethanol pilot plant at the Forestry and Forest Product Research Institute (Tsukuba, Ibaraki, Japan). The bioethanol pilot plant conducts soda-AQ cooking of Japanese cedar (*Cryptomeria japonica*), which generates black liquor as a byproduct. The soda-AQ conditions used at the plant are as follows: active alkaline charge of 19.5% on wood; AQ charge of 0.1% on wood; cooking time of 2 h; and cooking temperature of 170 °C. The solid content of the black liquor was 28.8% (w/w). The black liquor was dried to a powder by a spray dryer system (PJMSD-10SY, Powdering Japan) operating at a chamber temperature of 90 °C and an inlet air temperature of 180 °C. The dried black liquor powder was then removed from the spray dryer system and kept in a vacuum oven over phosphorus pentoxide (P_2O_5) for 24 h prior to use.

2-2 Methods

2-2-1 Preparation of purified lignin

Purified lignin was isolated from black liquor. To precipitate the lignin, the pH of black liquor was adjusted to 2.0 with 20% (w/w) sulfuric acid. The solution was then centrifuged to recover the precipitate, which was then washed with water. The centrifuging and washing procedure were repeated eight times. The precipitate was then vacuum-dried for 24 h and used as purified lignin.

2-2-2 Determination of Klason method

The primary hydrolysis stage was performed with 1 g of samples in 15 mL of 72% (w/w) H_2SO_4 for 2.5 h using a glass rod. The solution was then diluted to 4 wt% H_2SO_4 and autoclaved for 1 h at 121 °C (secondary hydrolysis stage). After all the carbohydrates were completely hydrolyzed, the solution was cooled and the residue (acid-insoluble lignin) was filtered on a 1G3. The acid-insoluble lignin was washed with water and dried for 24 h at 105 °C. The amount of acid-insoluble lignin was presented as the percentage of the oven-dry weight of each residue sample.

The amount of acid-soluble lignin remaining soluble in the 4 wt% H_2SO_4 solution after filtration of the acid-insoluble lignin was estimated by the ultraviolet (UV) spectroscopic method described in Tappi Method UM 250 um-83 (1991). Lignin's absorptivity of 110 $L \bullet g^{-1} \bullet cm^{-1}$ at 205 nm was used to estimate the concentration of lignin in each sample solution.

2-2-3 Evaluation of lignin content by UV method

A sample was dissolved in 1, 4-dioxane/0.2 M sodium hydroxide (NaOH; v/v = 1/1). The pH of the sample solution was adjusted to 5.0 with acetic acid. UV absorption (ABS) at 280 nm was determined using a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). The UV lignin content was calculated from the ABS coefficient of lignin (Dence 1992; Takahashi et al. 2014). The ABS coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration and UV absorbance of the purified lignin at 280 nm, which was 26.1 $L \bullet g^{-1} \bullet cm^{-1}$.

2-2-4 Chemical analysis of black liquor powder

The dried black liquor powder (10 g) was slowly dissolved in 50 mL of distilled water. The solution was titrated with 1 M hydrochloric acid (HCl) to determine its contents of sodium hydroxide and sodium carbonate.

3 Results and discussion

3-1 Total lignin content of raw material

The total lignin content of the raw materials (black liquor powder and purified lignin) used in this study is equal to the sum of their contents of acid-soluble lignin derived from the Klason method and acid-insoluble lignin (Klason lignin). The results for the black liquor powder indicated contents of 11.3% (w/w) acid-insoluble lignin and 7.9% (w/w) acid-soluble lignin derived from the Klason method, and the total lignin content of the black liquor powder was 19.2% (w/w). The results for the purified lignin indicated contents of 90.6% (w/w) acid-insoluble lignin and 7.1% (w/w) acid-soluble lignin derived from the Klason method, and the total lignin content of the purified lignin was 97.7% (w/w) (Table 2).

3-2 Absorption coefficient of soda lignin for evaluation of UV method

An ABS coefficient was determined for the Japanese cedar soda lignin, which was considered to be the origin of the lignin content of the purified lignin. Since lignin maximally absorbs UV light at 280 nm, the soda lignin calibration curve could be used to estimate the concentration of lignin in any solution of purified lignin, based on its ABS at 280 nm (Figure 11). The ABS coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration and UV absorbance of purified lignin at 280 nm. The ABS coefficient was 26.1 $L \cdot g^{-1} \cdot cm^{-1}$. The UV lignin content was calculated from the ABS coefficient.

3-3 Composition of black liquor powder

Sodium hydroxide and sodium carbonate are the major alkaline components of black liquor powder. The alkali content of black liquor powder was determined by titration with HCl. Figure 12 shows Formulas 1, 2, and 3 for the reactions of sodium hydroxide and sodium carbonate with HCl, and the titration curve. The reactions shown in Formulas 1 and 2 result in a change of the pH of the solution to about pH 9 after adding HCl. Sodium hydrogen carbonate produced by the addition of HCl to the sodium carbonate is also then titrated by HCl, as shown in Formula 2. The final pH of the solution reaches about pH 4 after adding HCl by the reaction shown in Formula 3. Taken together, the results showed that the black liquor powder consisted of sodium hydroxide (7.3%, w/w), sodium carbonate (66.7%, w/w), and lignin (18.0%, w/w) (Table 3).

Table 2. Total lignin contents of dried black liquor powder and purified lignin

	Klason lignin (%)	Acid-soluble lignin* (%)	Total lignin (%)
Black liquor powder	11.3	7.9	19.2
Purified lignin	90.6	7.1	97.7

*This lignin means an acid-soluble lignin derived from the Klason method.

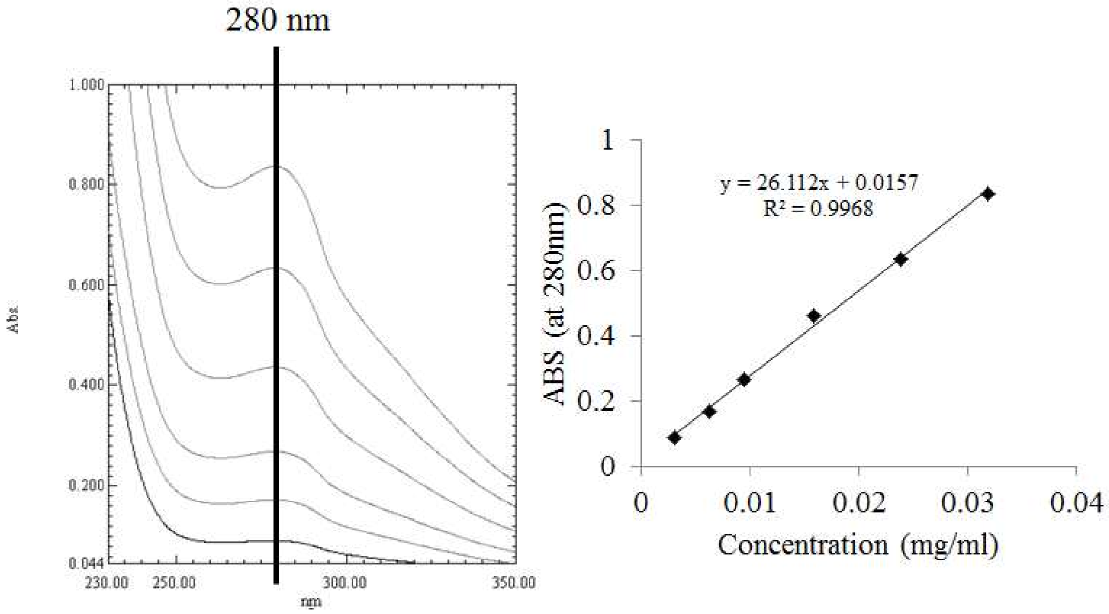
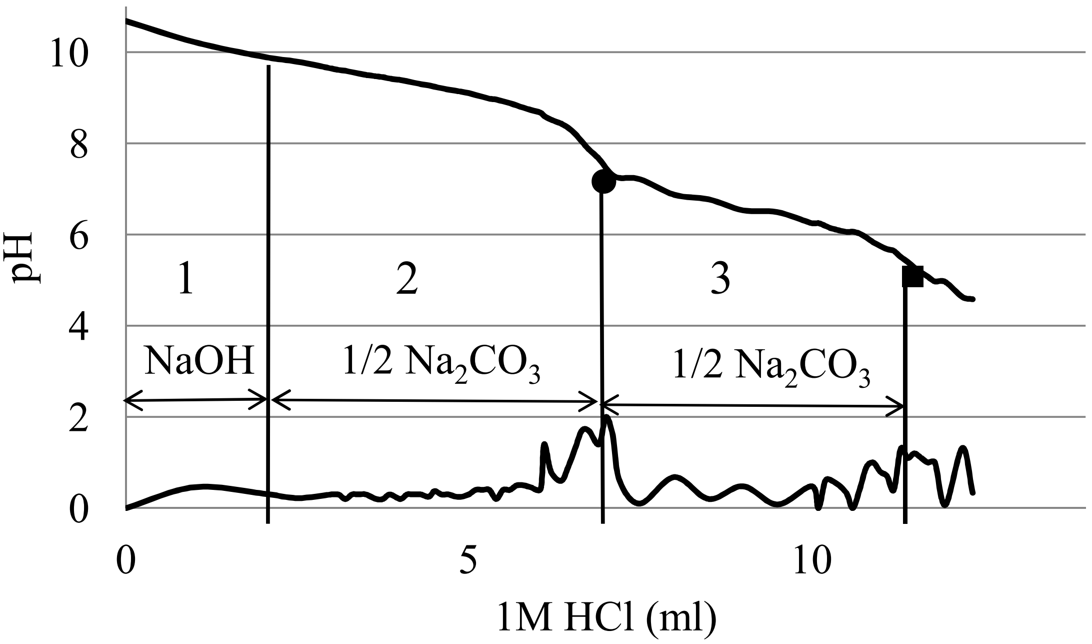


Figure 11. Absorption (ABS) coefficient of soda lignin as determined by UV spectroscopy



1 $NaOH + HCl \rightarrow NaCl + H_2O$

2 $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

3 $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Figure 12. Determination of the alkali content of dried black liquor powder by hydrochloric acid titration

Table 3. Composition of black liquor powder

Composition of black liquor powder		
NaOH %	Na_2CO_3 %	Lignin %
7.3	66.7	18.0

4 Conclusion

The black liquor powder used in this study was prepared from black liquor, which was dried to a powder using a spray dryer system. The total lignin content of each raw material (black liquor powder and purified lignin) used in this study is equal to the sum of their contents of acid-soluble lignin derived from the Klason method and the acid-insoluble lignin (Klason lignin). The total lignin content of the black liquor powder was 19.2% (w/w) and that of the purified lignin was 97.7% (w/w). The ABS coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration and UV absorbance of purified lignin at 280 nm. The ABS coefficient was 26.1 $L \cdot g^{-1} \cdot cm^{-1}$. The black liquor powder consisted of sodium hydroxide (7.3%, w/w), sodium carbonate (66.7%, w/w), and lignin (18.0%, w/w).

CHAPTER 3 Preparation and characterization of alkaline PEG-treated lignin from black liquor powder

1 Introduction

Technical lignins are divided into two categories (El Mansouri and Salvadó 2006). The first category includes sulfur-containing commercial lignins, such as kraft lignin and lignosulfonate. The second grouping is the non-sulfur lignins obtained from other pulping processes, such as soda, organosolv, steam explosion, and acid hydrolysis. During pulp manufacture, the lignin in black liquor is combusted to generate energy and recover chemicals. It has been reported that only about 2% of the byproduct lignin produced from industrial pulp manufacturing is utilized for purposes other than energy production (Gargulak and Lebo 2000). Approximately 1,000,000 tons/year of lignosulfonate originating from sulfite pulping, and less than 100,000 tons/year of kraft lignin produced from kraft pulping were utilized commercially (Gargulak and Lebo 2000; Gosselink *et al.* 2004). Technical lignins can be used as dispersants, binders, and surfactants (Dizhbite *et al.* 1999; Gargulak and Lebo 2000; Lora and Glasser 2002; Gosselink *et al.* 2004; El Mansouri and Salvadó 2006; Stewart 2008). The existing markets for technical lignins (predominantly lignosulfonates) are confined to low-value products or limited to very narrow market segments (Gosselink *et al.* 2004; Doherty *et al.* 2011). To develop additional applications for technical lignins, it is important to develop modification methods to enhance lignin properties for high-end value-added products.

One of the most important applications of lignin-based high value-added products is carbon fibers (CFs) (Kubo and Kadla 2004; 2005; Fernandes *et al.* 2006). Generally, commercial CFs, such as pitch-based CFs, are produced by a thermal melt spinning method in order to provide precursor fibers. To prepare lignin-based fibers following the industrial melt spinning process, the lignin should melt while being heated and should not be degraded by the heat. Since extensive cross-linking and strong intramolecular interactions of polymeric lignins constrain their utilization in solid material systems (Li *et al.* 1997), hardwood lignins are more easily processed than softwood lignins (Kadla and Kubo 2004). In the 2000s, Kadla *et al.* (2002) developed a process to derive kraft lignin-based CFs from hardwood without chemical modification. They prepared CFs by using hardwood kraft lignin with 5% polyethylene oxide (PEO) as a plasticizer. Polymer blending is a useful technique to improve the physical properties of technical lignins. In polymer blending systems, lignin generally increases the modulus and cold crystallization temperature, but it decreases the melt temperature (Doherty *et al*. 2011). Recently, Baker *et al*. (2012) developed kraft lignin-based CFs by using an organic solvent purification system applied to hardwood kraft lignins.

It is reported that softwood lignins, such as soda lignin, prepared from alkaline cooking are infusible (Kubo *et al.* 1997; 1998). To operate a softwood lignin-based CF production following the industrial melt spinning method, the lignin should have certain thermal melting characteristics. To obtain the desired thermal melting characteristics, the softwood lignin needs chemical modification or blending techniques. Norberg *et al.* (2013) and Nordström *et al.* (2013) reported the continuous spinning of softwood kraft lignin by adding a purified hardwood kraft lignin as a softening agent.

To change the thermal characteristics of softwood soda lignin, we successfully employed a new lignin modification method which used dried black liquor powder and polyethylene glycol (PEG). Black liquor powder was directly modified using PEG under alkaline conditions (termed as alkaline PEG treatment). This paper presents the alkaline PEG treatment, and the chemical and thermal characteristics of the derivatized lignin.

2 Experimental procedures

2-1 Materials

2-1-1 Black liquor powder

Black liquor was obtained from the bioethanol pilot plant at the Forestry and Forest Product Research Institute (FFPRI). The bioethanol pilot plant conducts soda-anthraquinone (AQ) cooking of Japanese cedar (*Cryptomeria japonica*), which generates black liquor as a byproduct. The soda-AQ conditions are as follows: active alkaline charge of 19.5% on wood; AQ charge of 0.1% on wood; cooking time of 2 h; cooking temperature of 170 °C. The solid content of the black liquor was 28.8%. The black liquor was dried to a powder by a spray dryer system (Powdering Japan PJMSD-10SY) operating at a chamber temperature of 90 °C and an inlet air temperature of 180 °C. The dried black liquor powder was then removed from the spray dryer system and kept in a vacuum oven over phosphorus pentoxide (P_2O_5) for 24 h prior to use.

2-2 Methods

2-2-1 Alkaline PEG treatment

The dried black liquor powder was dissolved in PEG solutions of various average molecular weights (200, 400, 600, 1000, and 2000), ethylene glycol (EG), or diethylene glycol (DEG). The mixture was transferred into a separable flask and heated to either 120 or 160 °C at atmospheric pressure for 2 h in an oil bath. After the reaction, the mixture was slowly poured into 500 mL of distilled water and the solution was acidified to pH 2.0 by 3 M HCl to produce a precipitate. The precipitate was filtered and the solids dried in a vacuum oven over P_2O_5.

2-2-2 Evaluation of lignin content

The lignin content of the alkaline PEG-treated lignin was measured using the UV method (Dence 1992; Takahashi *et al* 2014), which involved the following steps. A sample was dissolved in 1,4-dioxane/0.2 M sodium hydroxide (NaOH; v/v = 1/1). The pH of the sample solution was adjusted to pH 5.0 with acetic acid. The UV ABS at 280 nm was measured by a UV spectrophotometer (Shimadzu UV-1800). The UV lignin content was calculated from the ABS coefficient of lignin of 26.1 $L \cdot g^{-1} \cdot cm^{-1}$ at 280 nm.

2-2-3 Thermal melting characteristics

The thermal melting characteristics of the alkaline PEG-treated lignin were evaluated by a softening point system (Mettler Toledo DP 70). This part of the process was performed by increasing the temperature from 100 to 200 °C at the rate of 2 °C/min.

The alkaline PEG-treated lignin powder (200 mg) was filled into a cylinder loaded with a ball that had a mass of 4 g. The flow length of the melted sample was monitored by the system.

2-2-4 Nuclear magnetic resonance (NMR) analysis

The chemical structure of the lignin derivatives was estimated by NMR analysis. Alkaline PEG-treated lignin (200 mg) was dissolved in 600 μL of deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. The concentration of lignin solution was 20 to 30 wt.%. The ^{13}C-NMR spectrum of the lignin solution was recorded using a JEOL-500 MHz NMR spectrometer (Japan) operating at 125.65 MHz with proton noise decoupling. The spectrum was registered at 28 °C.

3 Results and discussion

3-1 Thermal melting characteristics of the alkaline PEG-treated lignin

Figure 13 demonstrates the thermal melting behavior of the alkaline PEG-treated lignins (PEG 1000 and PEG 2000 treatments) prepared at 120 °C. As shown in Fig. 13, the alkaline PEG-treated lignin gradually melted with heating. Figure 14 shows the melting length of the alkaline PEG-treated lignins (a: PEG 2000 and b: PEG 1000 treatments), which were made at 120 °C, by increasing the temperature at a rate of 2 °C/min. The thermal melting of the alkaline PEG-treated lignin made with PEG 2000 started at 102.5 °C (Fig. 14a). The melting length of the lignin sample increased steadily as the temperature rose, reaching 5 mm at 107.8 °C. At 122.5 °C, the sample dropped to the bottom of the test cylinder. On the other hand, the thermal melting speed of the alkaline PEG-treated lignin made from PEG 1000 was slower than that made from PEG 2000. The PEG 1000 lignin sample started melting at 116.2 °C, and the length reached 5 mm at 130.6 °C. At 167.6 °C, the sample dropped to the bottom of the test cylinder (Fig. 14b). The thermal melting characteristics of alkaline PEG lignin made from various molecular weight PEGs (*i.e.*, 200, 400, 600, 1000, and 2000) were checked and shown in Table 4. The melting characteristics of these derivatized lignins were evaluated by the flow length on the softening point system. The plus mark (+) in Table 4 indicated that the melting length of the sample was more than 5 mm, whereas the minus mark (-) indicated that the sample did not melt or that the melting length was less than 5 mm. In the alkaline PEG treatment at 120 °C, the samples for both PEG 1000 and PEG 2000 had desirable melting characteristics. However, derivatized lignins made with lower molecular weight PEG (*i.e.*, 600, 400, and 200) at 120 °C did not exhibit any of the desired melting characteristics. On the other hand, all derivatized lignin samples showed the desired melting characteristics when the PEG treatments were performed at 160 °C. The melting characteristics of the modified lignins were improved considerably by increasing the reaction temperature of alkaline PEG treatment. Figure 15 shows the melting lengths of the alkaline PEG-treated lignin made at 160 °C by using (a) PEG 400 and (b) PEG 1000. The thermal melting of alkaline PEG-treated lignin made with PEG 1000 started at 102.2 °C (Fig. 15b). The length reached 5 mm at 106.0 °C, and the sample dropped to the bottom of the test cylinder at 119.2 °C. When compared the T_s at which the length of the sample reached to 5 mm of PEG 1000-lignin treated at 120 °C and 160 °C, the later was 48.4 degree less than the former. For the PEG 400 treatment, the thermal melting of the derivatized lignin started at 134.1 °C with the length reaching 5 mm at 144.5 °C (Fig. 15a). These data indicate that the higher PEG reaction temperature with the higher PEG molecular weight improved the thermal melting characteristics and physical properties of lignin.

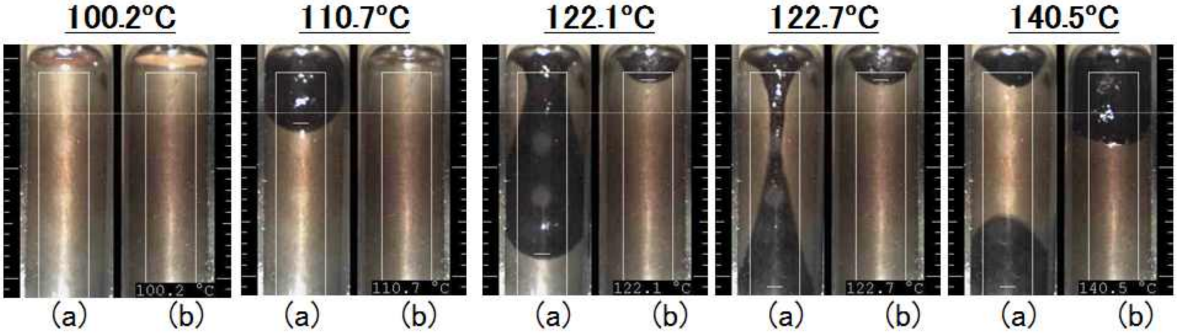


Figure 13. Thermal softening behavior of the alkaline PEG-treated lignin with elevating temperature to determine softening point (a) PEG 2000 treated and (b) PEG 1000 treated at 120 °C

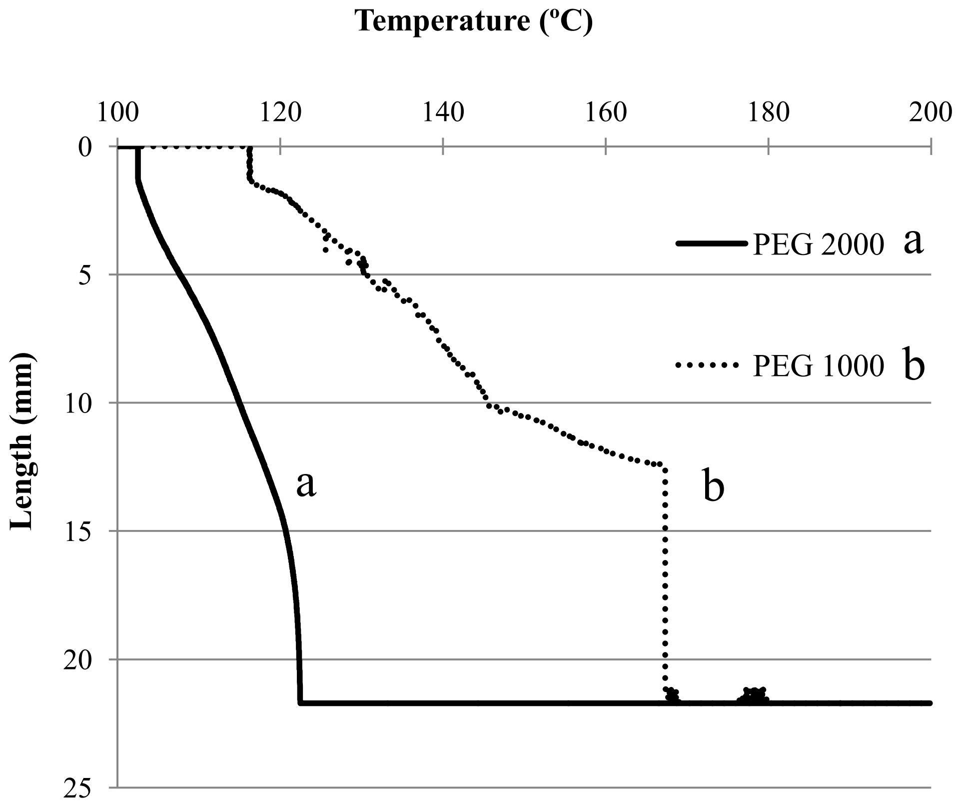


Figure 14. Thermal softening length of the alkaline PEG-treated lignins (Treatment temperature at 120 °C: (a) PEG 2000 and (b) PEG 1000)

Table 4. Thermal melting characteristics of the alkaline PEG-treated lignins

	Molecular weight of PEGs					Non-treated
Alkaline PEG treated lignin	200	400	600	1000	2000	
Treated at 120ºC	-	-	-	+	+	-
Treated at 160ºC	+	+	+	+	+	-

+ : the melting length of sample was greater than 5 mm,

- : did not melt or the melting length was less than 5 mm

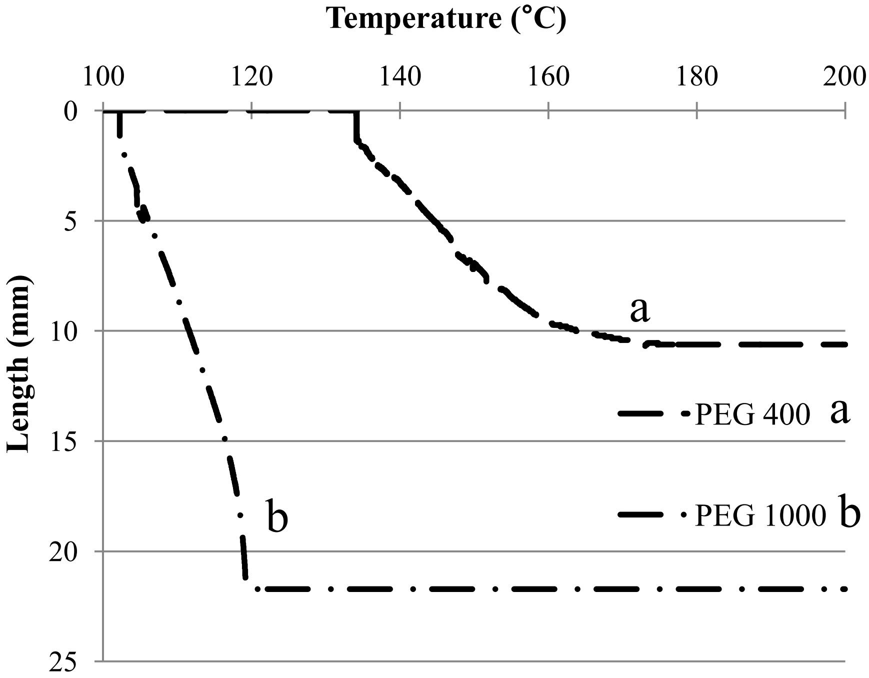


Figure 15. Thermal softening length of the alkaline PEG-treated lignins (Treatment temperature at 160 °C: (a) PEG 400 and (b) PEG 1000)

3-2 Effect of the reaction temperature of alkaline PEG treatment on grafting PEG onto lignin

The PEG content grafted into the soda lignin during the treatment was evaluated by determining the lignin content analysis of the samples. Figure 16 shows the lignin content of the alkaline PEG-treated lignins for various PEG molecular weights prepared at 120 °C (circle) and 160 °C (square). The lignin content of the alkaline PEG-treated lignin prepared at 120 °C decreased linearly with increasing molecular weight of PEG used in the reaction. The decrease in the lignin content indicated the increased amounts PEG being grafted onto the soda lignin. The lignin content of derivatives prepared at 160 °C was much lower than that of derivatives prepared at 120 °C. This indicated that a higher amount of PEG was introduced into the lignin when the grafting reaction temperature was performed at 160 °C. It should be noted that the better thermal melting characteristics of the lignin treated at 160 °C was attributable to the introduction of higher amounts of PEG.

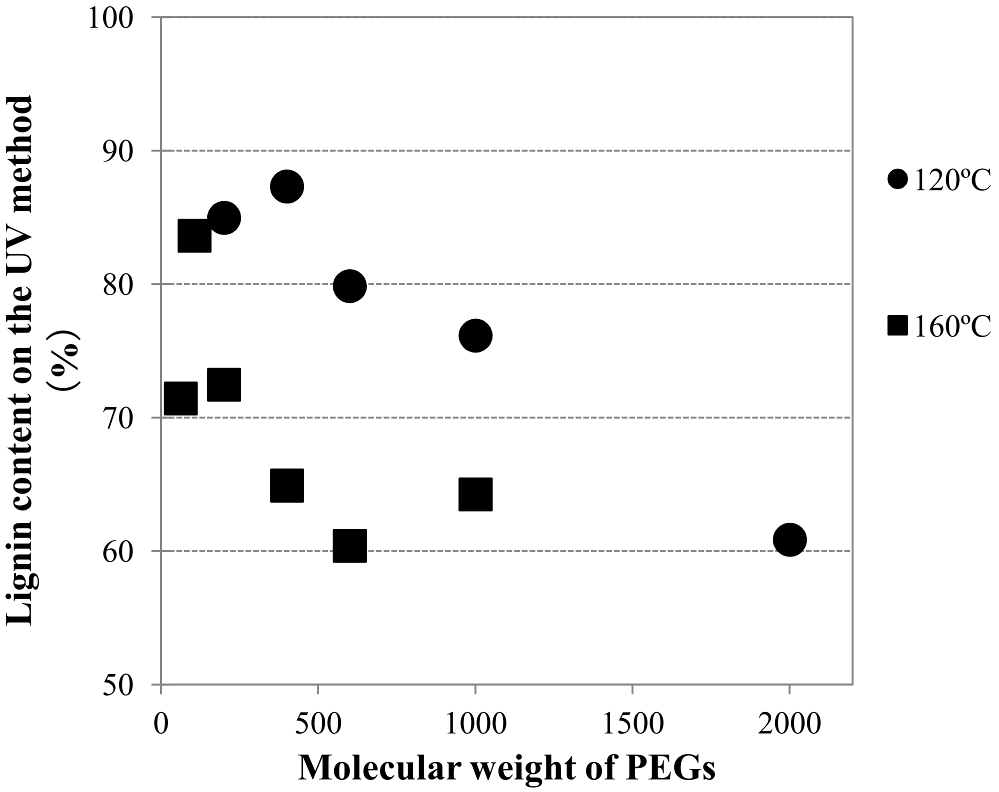


Figure 16. Effect of the PEG molecular weight on the lignin content of the alkaline PEG-treated lignin at 120 °C(●) and 160 °C(■)

3-3 Reaction mechanism of the alkaline PEG treatment of lignin

In the alkaline PEG treatment, since excess amount of PEG exixts around lignin molecules, possible reaction site on the lignin will be wholly reacted with PEG. If the number of possible reaction site did not increase in the reaction, then the relationship between the amount of introduced PEG and the size of PEG would be linear. Figure 16 showed a linear correlation between the lignin content in alkaline PEG-treated lignin prepared at 120 °C and the molecular weight of PEG. This suggested that the number of possible reaction sites on the lignin was limited and did not increase in the treatment at 120 °C. The alkaline PEG-treated lignin was analyzed using ^{13}C-NMR to clarify the bonded position of the PEG to the lignin. Figure 17 shows the ^{13}C-NMR spectrum of the alkaline PEG-treated lignin that was prepared using PEG 400 at 160 °C. The signal at 55.6 ppm was assigned to the carbon atoms of the methoxy groups of lignin. The strong signal at 69.8 ppm (b) was primarily assigned to the methylene carbons of the repeating unit of the PEG polymer. The signals at 72.3 ppm (a) and 60.2 ppm (d) were assigned to the methylene carbons of the alcoholic end groups of the PEG. These three signals (a, b, and d) could be detected even if unreacted PEG remained in the sample. In addition to these three signals, a small signal at 66.3 ppm (c) was assigned to methylene carbons bonded to the alpha carbon on the lignin side chain *via* an ether linkage (Kishimoto *et al.* 2004). This data strongly suggested that PEG is grafted to the lignin with an ether bond at the α-carbon of the lignin, as shown in Fig. 17.

Figure 18 shows a proposed reaction mechanism between the soda lignin and the PEG polymer under alkaline treatment conditions. In general, there are few alcoholic hydroxyl group on the benzyl position (α-carbon position) of soda or kraft lignin (Adler and Hernestam 1955). However, the NMR spectrum in Fig. 17 shows the chemical structure of the lignin with the PEG bonded at its α-carbon position.

Under the alkaline condition, lignin containing free phenolic hydroxyl groups were deprotonated and released the hydroxyl groups at the α-carbon position to form the quinone methides. The terminal hydroxyl group in PEG should react with the quinone methides in the lignin at α-carbon position.

The higher amounts of PEG introduced onto the lignin at 160 °C suggested that the number of reaction sites in the soda lignin increased with increasing reaction temperatures. The vanillin yields from the alkaline nitrobenzene oxidation of soda-AQ lignin were 9% based on lignin content (Takahashi *et al.* 2014). This indicated that the soda-AQ lignin has possible reaction sites at α-carbon position. Thus, the alkaline PEG-treated lignin prepared at 160 °C had higher amounts of PEG than that prepared at 120 °C.

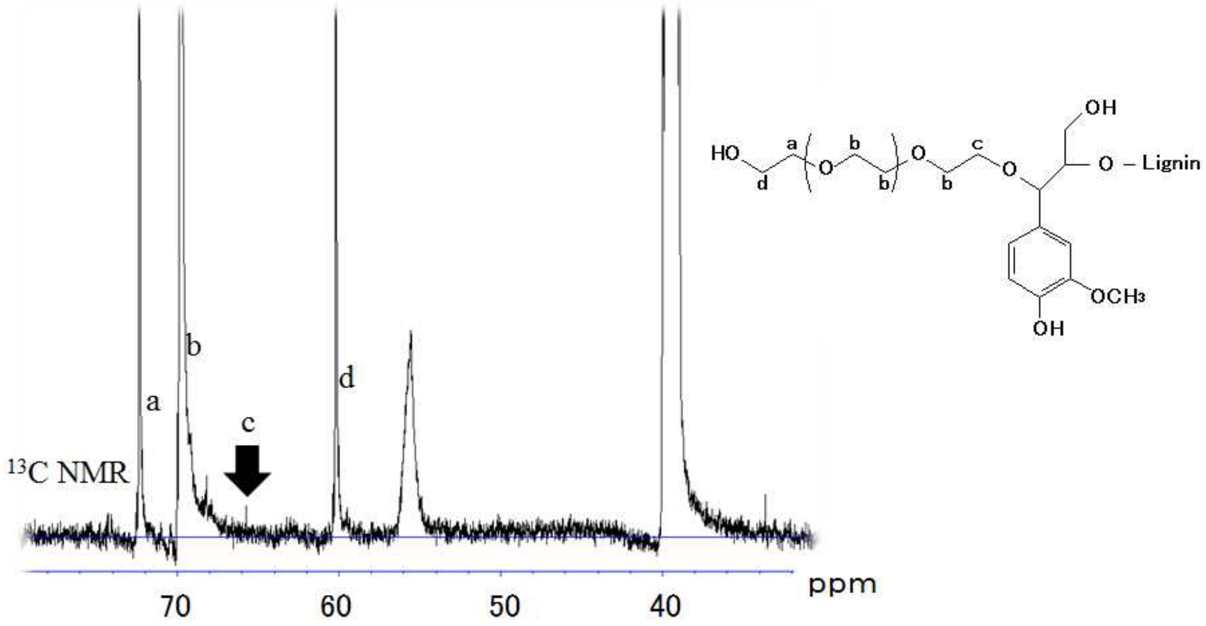


Figure 17. ^{13}C－NMR spectrum of alkaline PEG-treated lignin prepared from black liquor powder with PEG 400

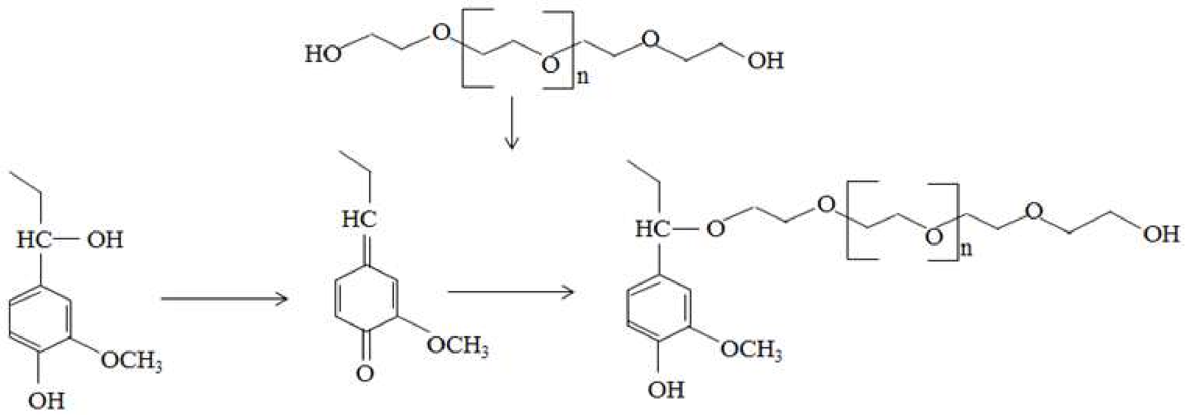


Figure 18. A reaction mechanism between soda lignin and PEG in the alkaline PEG treatment

4 Conclusion

1. The alkaline PEG-treated lignin from a softwood soda-AQ black liquor powder showed thermal melting characteristics with heating.

2. At the 120 °C alkaline PEG treatment, the samples made from PEG 1000 and PEG 2000 showed thermal melting; however, the samples using lower PEG molecular weights (*i.e.*, 600, 400, and 200) did not exhibit significant thermal melting. On the other hand, for the 160 °C alkaline PEG treatment, all samples showed thermal melting.

3. The treatment temperature and molecular weight of PEG had considerable effects on the physical properties of the alkaline PEG-treated lignin. The better melting characteristics of the 160 °C-treated lignin could be due to the higher amount of PEG grafted onto the soda-AQ lignin. The NMR data suggested that the PEG grafted to α-carbon of lignin *via* an ether linkage.

Chapter 4 Preparation and characterization of alkaline PEG-treated lignin from purified and acid-soluble lignin (Model experiment)

1 Introduction

Lignin is a major component in wood cell walls and can be isolated from wood *via* chemical pulping. Wood can be regarded as a lignin plastic reinforced by cellulose fibers (Hoyt and Goheen 1971). Many million tons of wood are processed annually in the chemical pulping industry to separate lignin from cellulose fibers. Spent liquors (black liquor) from pulping operations such as kraft, soda, and sulfite processes are some of the available sources of lignin. Lignins prepared from the black liquor of industrial pulping processes is called technical lignins. Some types of technical lignin can be used as dispersants, binders, and surfactants (Dizhbite *et al.* 1999; Gargulak and Lebo 2000; Lora and Glasser 2002; Gosselink *et al.* 2004; El Mansouri and Salvadó 2006; Stewart 2008; El Mansouri *et el.* 2011). However, only approximately 2% of the technical lignin produced from industrial pulp manufacturing is utilized for commercial purposes (Gargulak and Lebo 2000). In the industrial pulping process, most of the lignin in black liquor is combusted to generate energy and recover chemicals. To activate the commercial utilization of lignin, the mechanical properties of technical lignin must be improved, a key point in the preparation of these value-added products.

Polymer blending is a simple modification method to used to upgrade the thermoplastic properties of lignin (Feldman *et al.* 1995; Feldman 2002). Li *et al.* (1997) reported that lignin-based polymeric materials blended with polyvinyl acetate exhibited improved mechanical and thermoplastic properties. Kadla and Kubo (2004) prepared a blended polymer with a low T_g and a T_s using soda lignin and polyethylene terephthalate.

Chemical derivatization is a direct approach for improving the physical and chemical properties of lignin. Fang *et al.* (2011) reported that dicarboxylic acid prepared by dimerizing unsaturated fatty acids can be reacted with lignin *via* esterification, leading to the formation of lignin derivatives that could remove the rigidity and improve the flexibility of lignin. Although the physical and chemical properties of lignin can be improved *via* chemical derivatization, the cost of treatment is prohibitive on a commercial basis.

CF is a high-value added product that can be prepared from lignin (Kubo and Kadla 2004; 2005; Fernandes *et al.* 2006; Shen *et al.* 2011). For efficient lignin-based CF preparation, lignin can be converted into in fibers *via* melt-spinning. Lignin-based CF was first prepared from technical lignin blended with polyvinyl alcohol by Otani *et al.* (1969). Sudo *et al.* (1993) developed CF from a hardwood steam-exploded lignin, which was modified to a thermal melting material by phenolation. Uraki *et al.* (1995) produced a lignin fiber that was suitable for CF production *via* melt-spinning using hardwood organosolv lignin obtained from aqueous acetic acid pulping. In the 2000s, Kadla *et al.* (2002) developed a process to prepare hardwood kraft lignin-based CF without chemical modification. They prepared hardwood kraft lignin-based fibers using 5% polyethylene oxide (PEO) as a plasticizer. Recently, Baker *et al.* (2012) developed a method for producing lignin-based CF from purified hardwood lignin. Because the thermal processability of technical hardwood lignin is better than that of technical softwood lignin, the majority of lignin-based CF studies have been performed on hardwood lignin.

Kubo *et al.* (1997) reported that softwood lignins, such as soda lignin, prepared by alkaline cooking are infusible. Infusible softwood lignin can be made fusible by removing 30% of the high molecular mass fraction (Kubo *et al.* 1998). Recently, Norberg *et al.* (2013) and Nordström *et al.* (2013) reported the continuous spinning of softwood kraft lignin by adding purified hardwood kraft lignin as a softening agent.

In Chapter 3, I explained a simple softwood lignin modification method using a dried black liquor powder as a starting material. Spray-dried black liquor powder was directly treated with PEG under alkaline conditions (alkaline PEG treatment) (Yoon *et al.* 2015). The alkaline PEG-treated lignin prepared from black liquor powder exhibited its thermal melting property to be a CF precursor. The present study aimed to clarify the reaction of softwood lignin in the alkaline PEG treatment by model experiments using purified and acid-soluble lignin.

2 Experimental procedures

2-1 Materials

2-1-1 Black liquor powder

Black liquor was obtained from Japanese cedar (*Cryptomeria japonica*) wood chips *via* soda-AQ cooking. The soda-AQ conditions were as follows: active alkaline charge of 19.5% of wood, AQ charge of 0.1% of wood, cooking time of 2 h, and cooking temperature of 170 °C. Black liquor was dried to a powder using a spray dryer system (Powdering Japan PJMSD-10SY, Japan) operating at a chamber temperature of 90 °C and an inlet air temperature of 180 °C. The dried black liquor powder was then removed from the spray dryer system and kept in a vacuum oven over phosphorus pentoxide for 24 h prior to use (Yoon *et al.* 2015).

2-1-2 Purified lignin

Purified lignin (acid-insoluble lignin) was isolated from black liquor powder. The black liquor powder was dissolved in distilled water until it comprised 40% of the solution's content. The pH of this solution was then adjusted to 2 with 20% sulfuric acid to precipitate the acid-insoluble part. The solution was then centrifuged to recover the precipitate, and the precipitate was washed with water. The centrifuging and washing procedures were repeated eight times. The precipitate was then vacuum-dried for 24 h and used as purified lignin (acid-insoluble lignin).

2-1-3 Acid-soluble lignin fraction

The acid-soluble lignin fraction was extracted from the filtrate of the precipitation solution of the purified lignin preparation. The pH of the filtrate was adjusted to 7 with sodium hydroxide. Water in the filtrate was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h. After stirring for three days, the dried material was extracted with 1,4-dioxane. The insoluble material in the solution was filtered out, and the dioxane in the filtrate was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h. The dried material was extracted with chloroform using a shaking apparatus; the chloroform layer was then separated using a separating funnel. Chloroform in the chloroform layer was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h and used as the acid-soluble lignin fraction.

2-2 Methods

2-2-1 Alkaline PEG treatment of black liquor powder

Black liquor powder was directly modified using PEG under alkaline conditions (termed as alkaline PEG treatment) following the method used in our previous study (Yoon *et al.* 2015). The black liquor powder (30 g) was dissolved in PEG 1000 (150 g). The mixture was transferred to a separable flask and heated to 160 °C at atmospheric pressure in an oil bath. After the reaction, the mixture was slowly poured into 500 mL of distilled water and the solution was acidified to pH 2.0 with 3 M HCl to produce a precipitate. The precipitate was filtered and dried in a vacuum oven.

2-2-2 Alkaline PEG treatment of the purified lignin

A model experiment was carried out to clarify the reaction of lignin in the alkaline PEG treatment of the black liquor powder. The black liquor powder consisted of sodium hydroxide (7.3%), sodium carbonate (66.7%), and lignin(18.0%) (Chapter 2). The purified lignin was used as a model compound. The purified lignin (20 g) was mixed with sodium hydroxide (5 g) and sodium carbonate (50 g). The mixture was dissolved in 375 g of various average molecular weights of PEG (200, 300, 400, 600, 1000, 1500, and 2000), EG, or DEG. The solution was transferred into a separable flask (500 mL) with mechanical stirring and heated to 160 °C at atmospheric pressure in an oil bath. After the reaction, the reactant was slowly poured into 500 mL of distilled water and the solution was acidified to pH 2.0 with 3 M hydrochloric acid to produce a precipitate. The precipitate was filtered, and the solids were dried in a vacuum oven.

2-2-3 Evaluation of lignin content

The lignin content of the alkaline PEG-treated lignin was measured using the UV method (Dence 1992; Takahashi *et al*. 2014). Since the composition of the alkaline PEG-treated lignin consists of two components, only one of which (the lignin) absorbs in the UV spectral region, the lignin content measured by the UV method will reflect the amount of lignin in alkaline PEG treated sample. A sample was dissolved in 1,4-dioxane/0.2 M sodium hydroxide (NaOH; v/v = 1/1). The pH of the sample solution was adjusted to 5.0 with acetic acid. UV ABS at 280 nm was determined using a UV spectrophotometer (Shimadzu UV-1800, Japan). The lignin content was calculated from the ABS coefficient of lignin (UV lignin content). The ABS coefficient of the lignin was determined by the following process. The total lignin content of the purified lignin was determined using the Klason lignin method (TAPPI T222 om-02 2006), and the acid-soluble lignin derived from the Klason method was determined using the TAPPI useful method UM 250 um-83 (1991). The ABS coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration based on the total lignin content and UV absorbance of the purified lignin at 280 nm, which was 26.1 L•g^{-1}•cm^{-1}.

2-2-4 Thermal melting characteristics

The thermal melting characteristics of the alkaline PEG-treated lignin were evaluated using a softening point system (Mettler Toledo DP 70 Dropping poin system, Switzerland). The alkaline PEG-treated lignin powder (200 mg) was poured into a cylinder loaded with a ball of mass 4 g. The thermal melting test was performed by increasing the temperature from 100 to 200 °C at a rate of 2 °C/min. The flow length of the melted sample was monitored by the system.

2-2-5 Thermomechanical analysis (TMA)

TMA was performed using a TMA Q400 (TA Instruments, USA) at temperatures from 20 to 320 °C at a compression loading of 0.05 N under a N_2 stream at 50 mL/min. The values T_g and T_s were estimated as the first and the second transition points in the TMA curves, respectively.

2-2-6 Nuclear magnetic resonance (NMR) analysis

The chemical structures of lignin derivatives were estimated using NMR analysis. Alkaline PEG-treated lignin (200 mg) was dissolved using 600 μL of deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent. The concentration of the lignin solution was 20 to 30 wt.%. The ^{13}C-NMR spectrum of the lignin solution was recorded using a JEOL-500 MHz NMR spectrometer (JEOL, Japan) operating at 125.65 MHz with proton noise decoupling. The spectrum was registered at 28 °C.

3 Results and dicussion

3-1 Effect of the PEG molecular weight

The amount of PEG introduced into lignin during treatment was evaluated by determining the UV lignin content of the sample. Figure 19 shows the lignin content of the alkaline PEG-treated lignins using various PEG molecular weights prepared from purified lignin. The lignin content decreased with increasing PEG molecular weight. The decrease in lignin content indicated that increased amounts of PEG were being introduced into the purified lignin.

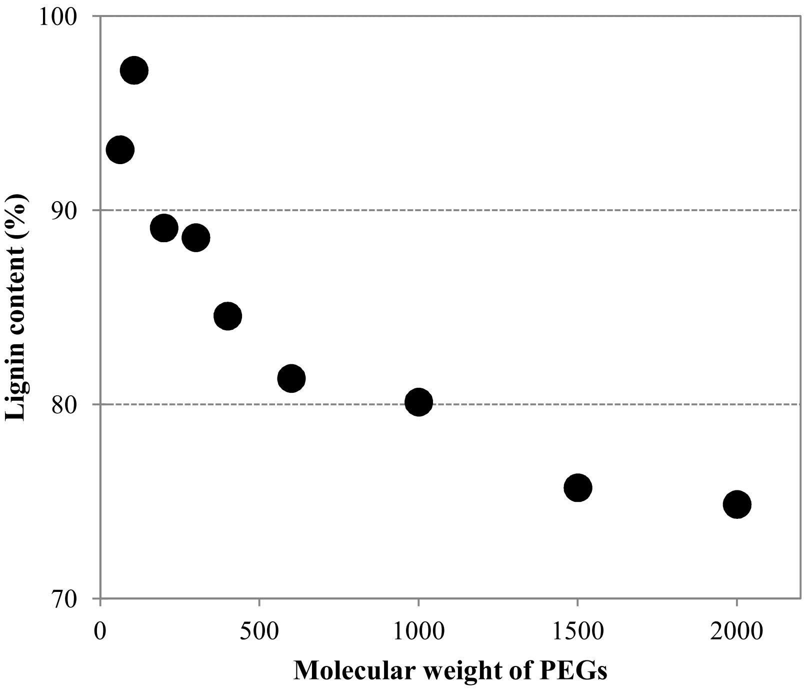


Figure 19. Effect of PEG molecular weight on the lignin content of alkaline PEG-treated lignin prepared from purified lignin

3-2 Thermal melting characteristics of alkaline PEG-treated lignin

Figure 20 and 21 demonstrates the thermal melting behavior of the alkaline PEG-treated lignin prepared from purified lignin (Fig. 20) and black liquor powder (Fig. 21) and the softening point that was determined with increasing temperature. As shown in Fig. 20 and 21, the alkaline PEG-treated lignin gradually melted with heating.

Figure 22 shows the melting length of the alkaline PEG-treated lignin prepared from black liquor powder, with the temperature increasing at a rate of 2 °C/min. The alkaline PEG-treated lignin prepared from black liquor powder started melting at 102.2 °C, and the length reached 5 mm at 105.3 °C. At 119.2 °C, the sample dropped to the bottom of the test cylinder. The thermal melting speed of the alkaline PEG-treated lignin prepared from purified lignin was slower than that of the lignin prepared from black liquor powder. Figure 23 shows the melting length of the alkaline PEG-treated lignin prepared from the purified lignin, with the temperature increasing at a rate of 2 °C/min. The thermal melting of the alkaline PEG-treated lignin prepared from the purified lignin started at 151.3 °C. The melting length of the lignin sample steadily increased as the temperature increased, reaching 5 mm at 179.2 °C. The thermal melting characteristics of the alkaline PEG-treated lignin prepared from various molecular weight PEGs (*i.e.*, 200, 300, 400, 600, 1000, 1500, and 2000), EG, and DEG were checked and are shown in Table 5. The melting characteristics of these alkaline PEG-treated lignin types were evaluated by flow length in the softening point system. The "+" in Table 5 indicates that the melting length of the sample was more than 5 mm, whereas the "–" indicates that the sample did not melt or that the melting length was less than 5 mm.

Figure 24, 25, and 26 shows the TMA curves of various lignin samples. These alkaline PEG-treated lignin types were prepared in the PEG 1000 series (Fig. 25, and 26). Thermal properies such as T_g and T_s were determined using TMA (Kubo et al. 1996). As shown in Fig. 24, the TMA curve of the purified lignin showed a decrease in dimension change starting at approximately 140 °C. This decrease continued until the temperature reached 220.4 °C, and was followed by a marked increase. During the dimension change-increasing step, the sample swelled and formed a foaming, rigid solid with thermo-setting. This result indicates that these samples were difficult to melt under heat. Because the purified lignin did not exhibit thermal melting characteristics (Table 5), its TMA curve can be regarded as a typical TMA plot of lignin samples that do not show thermal melting. As shown in Fig. 25, the TMA curve of the alkaline PEG-treated lignin prepared from black liquor powder was quite different from that of purified lignin (Fig. 24). The TMA curve (Fig. 25) showed a T_g at 157.4 °C, and the dimension change decreased rapidly to approximately 190 °C. After this rapid decrease, the decreasing ratio slowed. The TMA curve (Fig. 25) suggested that the alkaline PEG-treated lignin prepared from black liquor powder exhibited a thermal melting property (Kubo et al. 1996).

As shown in Fig. 26, the TMA curve of the alkaline PEG-treated lignin prepared from purified lignin showed T_g at 145.4 °C (Fig. 26). The decrease in dimension change continued until 184.3 °C, followed by a marked increase. This type of TMA curve (Fig. 26) is similar to that of purified lignin (Fig. 24) and does not show thermal melting on the softening point analysis system. This suggests that the alkaline PEG-treated lignin prepared from purified lignin did not show appropriate thermal melting performance during TMA analysis. However, the alkaline PEG-treated lignin prepared from purified lignin exhibited a thermal melting property in the softening point analysis system (Table 5). Because the dimension change of the alkaline PEG-treated lignin prepared from purified lignin dropped at a temperature approximately 30 °C lower than that of purified lignin, the lignin showed more than 5 mm of flow on the softening point analysis system (Fig. 24).

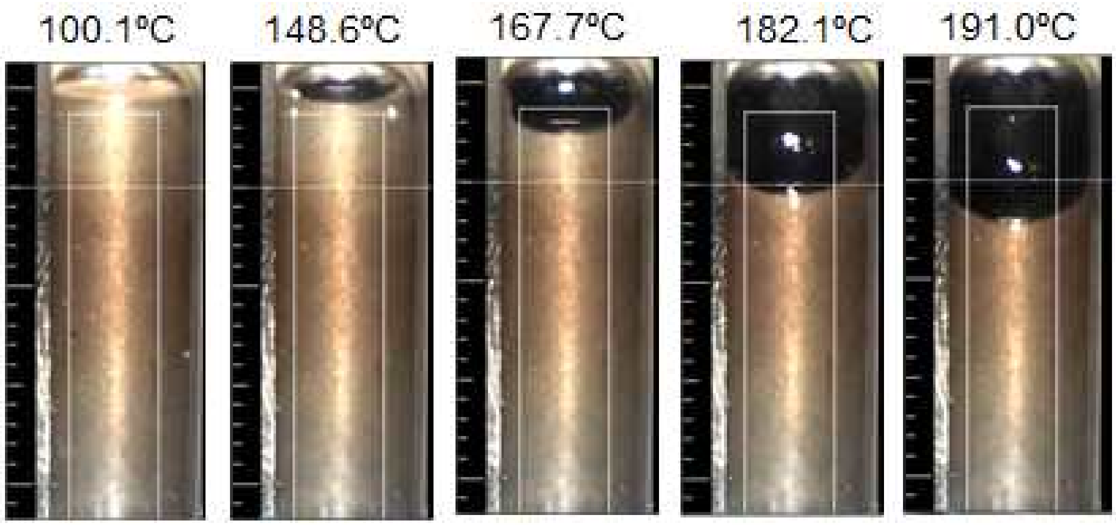


Figure 20. Thermal softening behavior of alkaline PEG-treated lignin prepared from purified lignin with increasing temperature to determine softening point

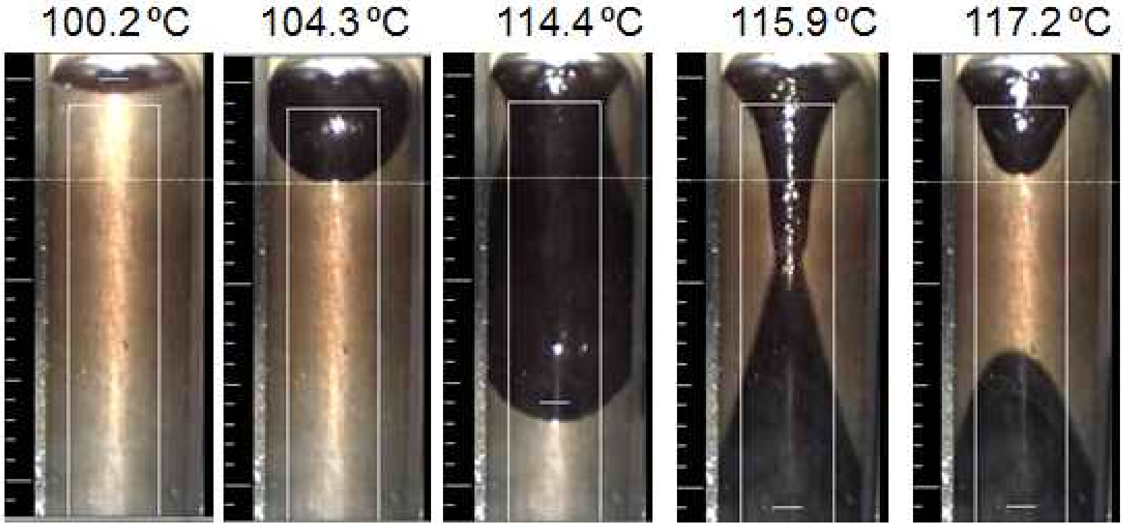


Figure 21. Thermal softening behavior of alkaline PEG-treated lignin prepared from black liquor powder with increasing temperature to determine softening point

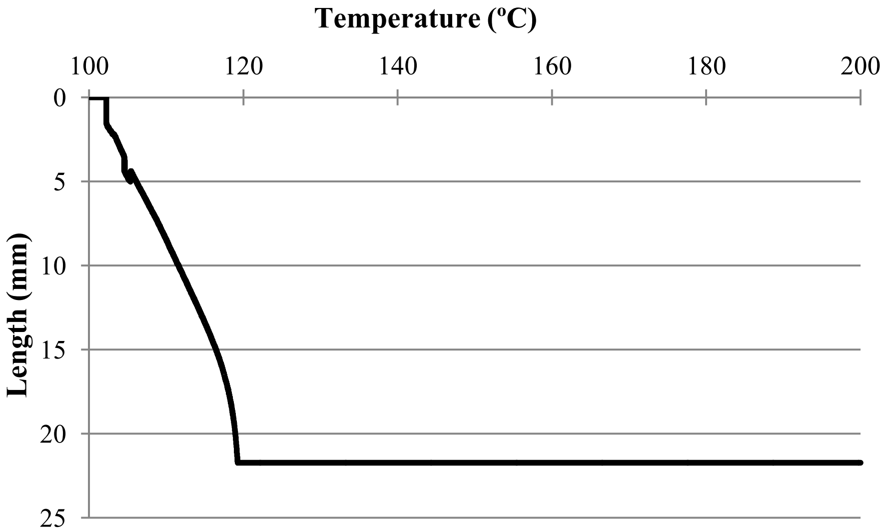


Figure 22. Thermal softening length of alkaline PEG-treated lignin prepared from black liquor powder

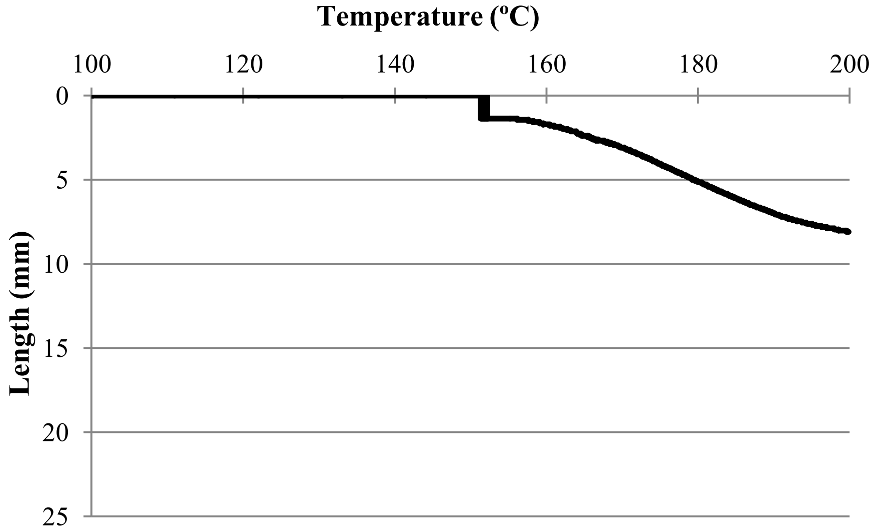
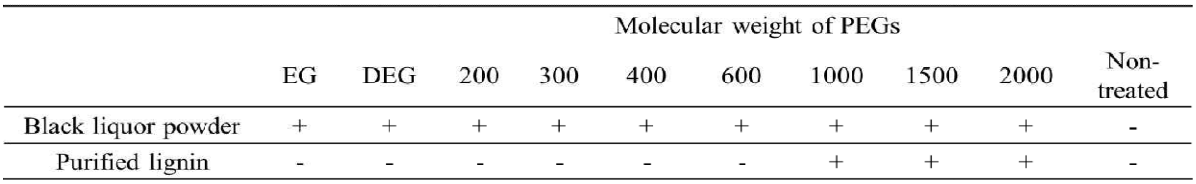


Figure 23. Thermal softening length of alkaline PEG-treated lignin prepared from purified lignin

Table 5. Thermal melting characteristics of alkaline PEG-treated lignin prepared from black liquor powder and purified lignin



	Molecular weight of PEGs									
	EG	DEG	200	300	400	600	1000	1500	2000	Non-treated
Black liquor powder	+	+	+	+	+	+	+	+	+	-
Purified lignin	-	-	-	-	-	-	+	+	+	-

+ : the melting length of sample was greater than 5 mm,
- : did not melt or the melting length was less than 5 mm
EG : Ethylene glycol,
DEG : Diethylene glycol

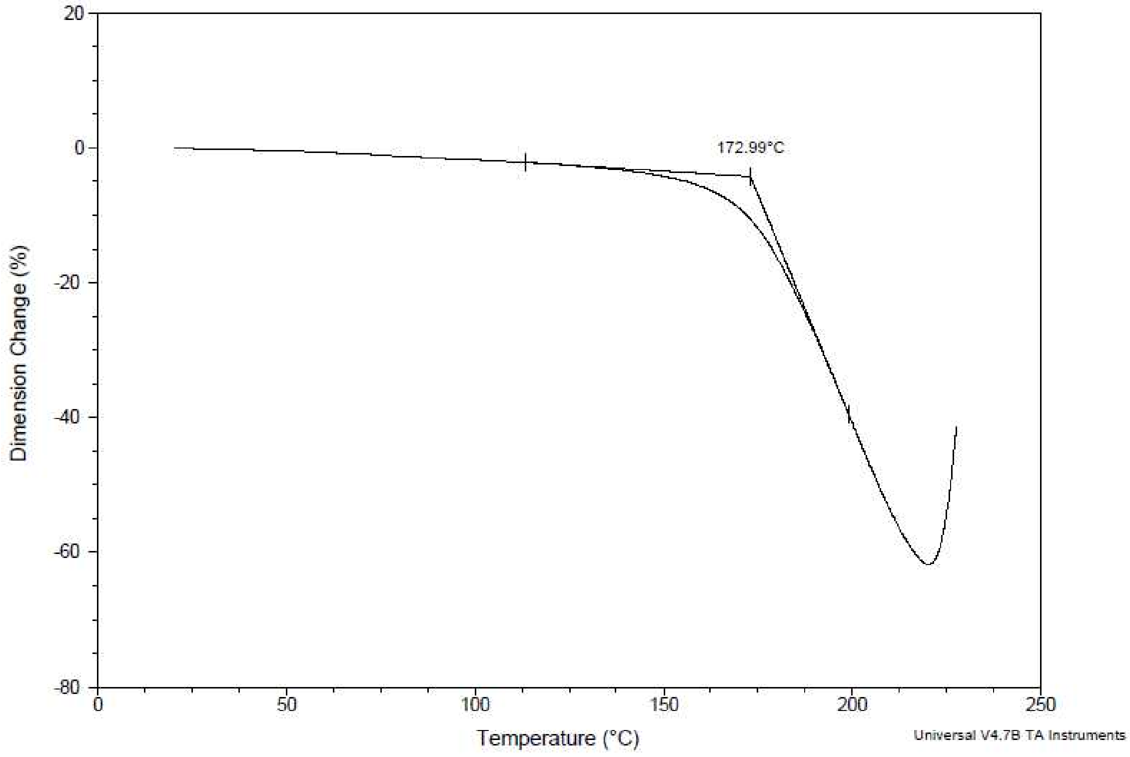


Figure 24. Thermal mechanical analysis of purified lignin

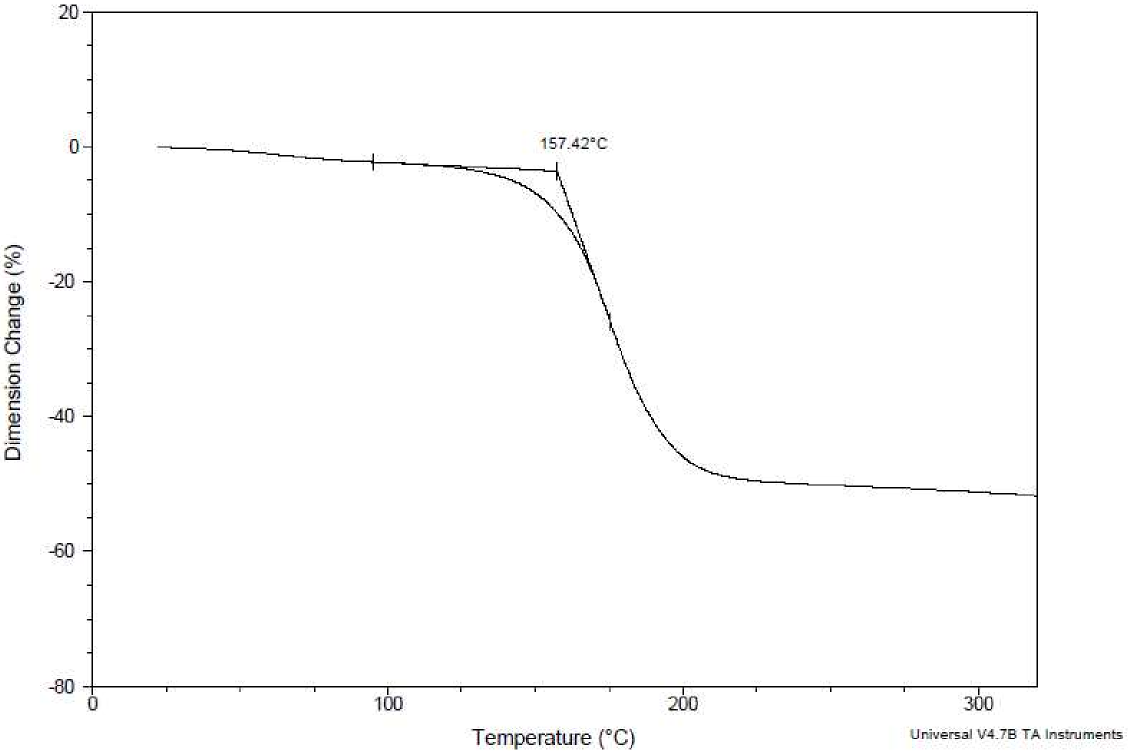


Figure 25. Thermal mechanical analysis of alkaline PEG-treated lignin prepared from black liquor powder

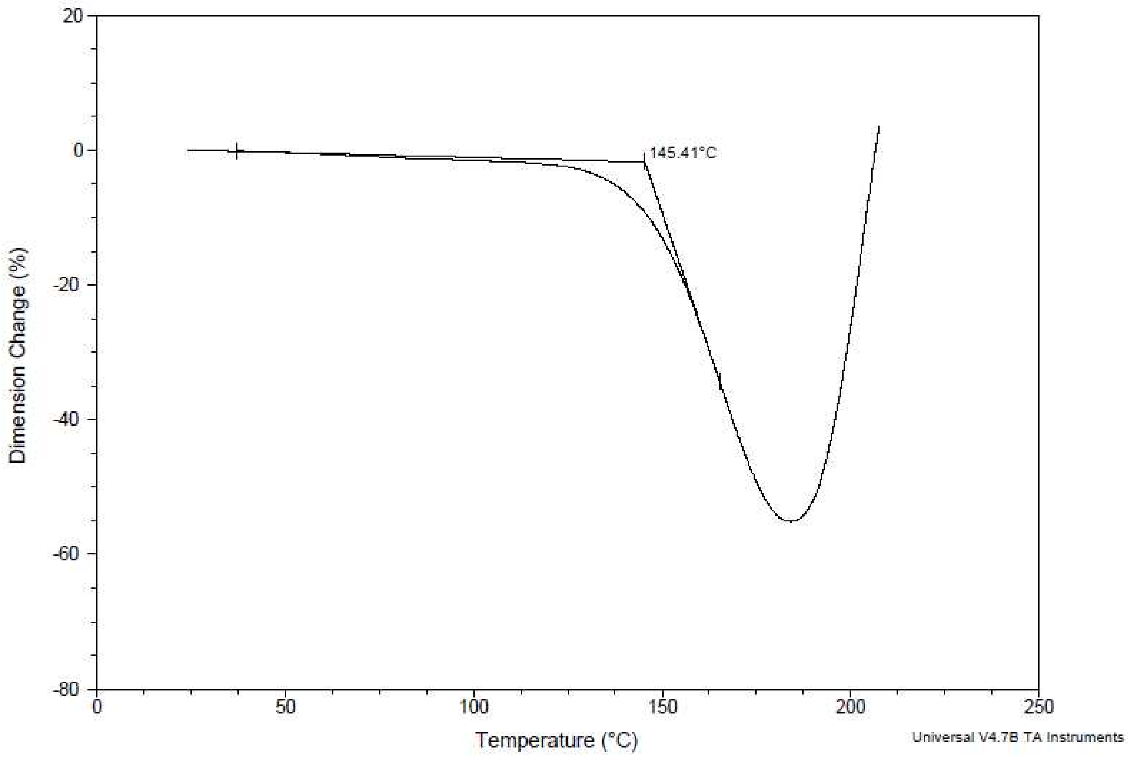


Figure 26. Thermal mechanical analysis of alkaline PEG-treated lignin prepared from purified lignin

3-3 Chemical structure of alkaline PEG-treated lignin

The alkaline PEG-treated lignin was analyzed using ^{13}C-NMR to clarify the bonded position of the PEG to the lignin. Figure 17, 27, 28, 29, and 30 shows the ^{13}C-NMR spectra of the purified lignin (Fig. 27), the alkaline PEG-treated lignin prepared from the purified lignin in PEG 200 (Fig. 28), PEG 400 (Fig. 29), PEG 1000 (Fig. 30), and the alkaline PEG-treated lignin prepared from black liquor powder in PEG 400 (Fig. 17). Signal assignment was reported in previous chapter (chapter 3). The signal at 55.6 ppm (e) was assigned to the carbon atoms of the methoxy groups of lignin. The strong signal (b) at 69.8 ppm was primarily assigned to the methylene carbons of the repeating unit of a PEG polymer. The signals at 72.3 ppm (a) and 60.2 ppm (d) were assigned to the methylene carbons of the alcoholic end-groups of PEG. These three signals (a, b, and d) could be detected even if unreacted PEG remained in the sample. In addition to these three signals, a small signal (c) at 66.3 ppm was assigned to the methylene carbons bonded to α-carbon on the lignin side-chain *via* an ether linkage (Kishimoto *et al.* 2004). These data strongly suggest that PEG was grafted to the lignin with an ether bond at the α-carbon of lignin. As shown in Fig. 17, the alkaline PEG-treated lignin prepared from black liquor powder showed the signal (c). However, this signal was not detected in the spectra of the alkaline PEG-treated lignin prepared from purified lignin (Fig. 28, 29, and 30). These data suggest that there was no linkage between lignin and PEG on the alkaline PEG-treated lignin prepared from purified lignin. This suggested that the data shown in Fig.19 of increasing amount of introduced PEG with increasing molecular weight of PEG might due to the unreacted PEGs in the sample. Generally, a higher molecular weight of PEG will result in stronger interaction between PEG and the other polymeric materials (Pillin *et al.* 2006). Removing of the unreacted higher molecular weight fraction of PEG would be difficult.

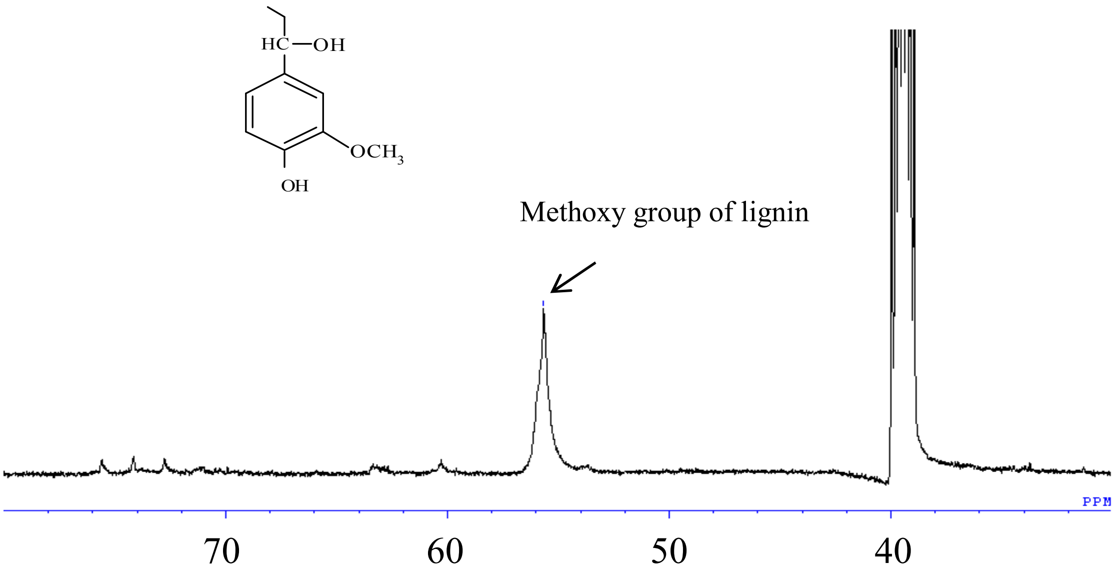


Figure 27. ^{13}C-NMR spectrum of purified lignin

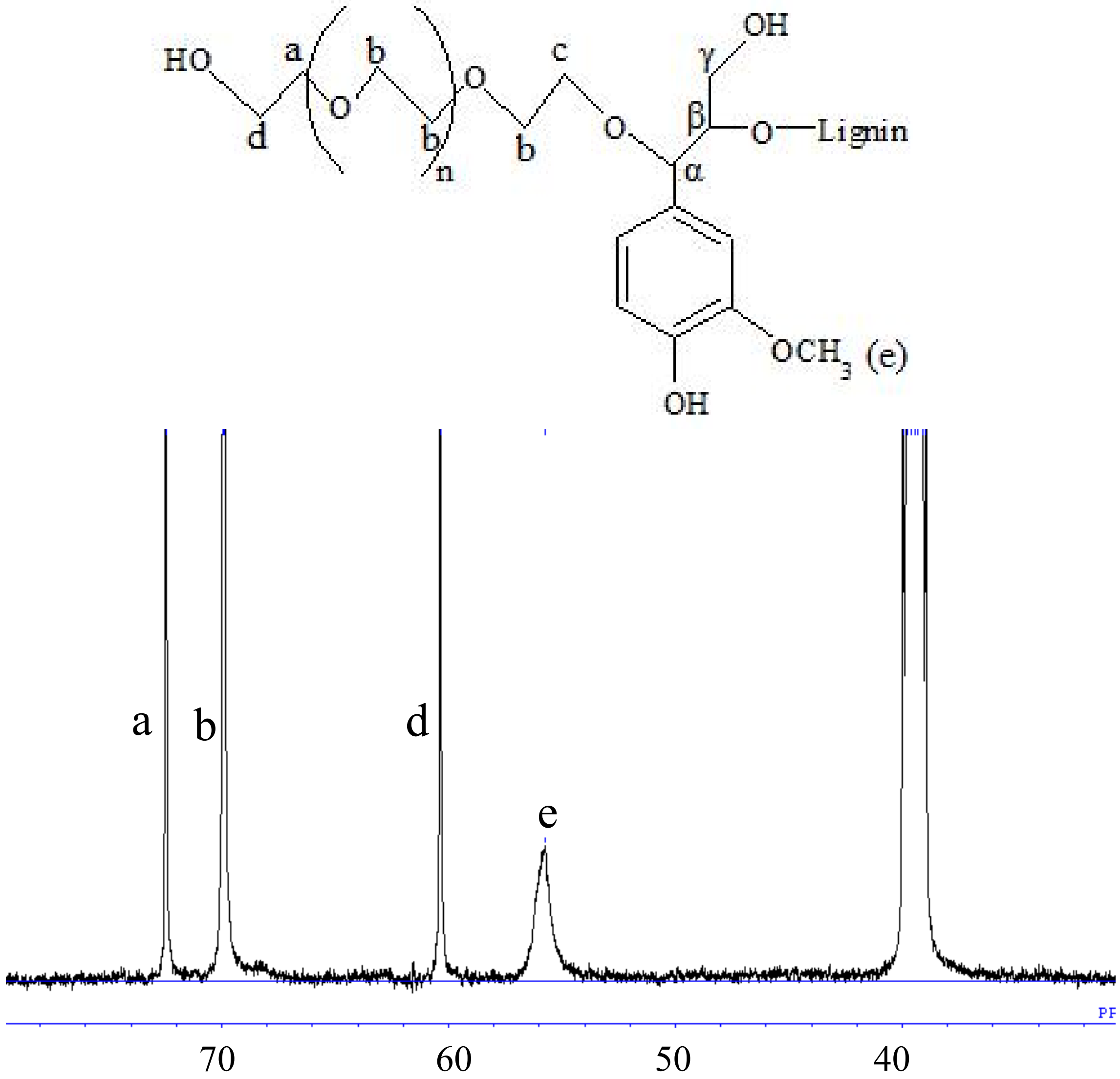


Figure 28. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 200

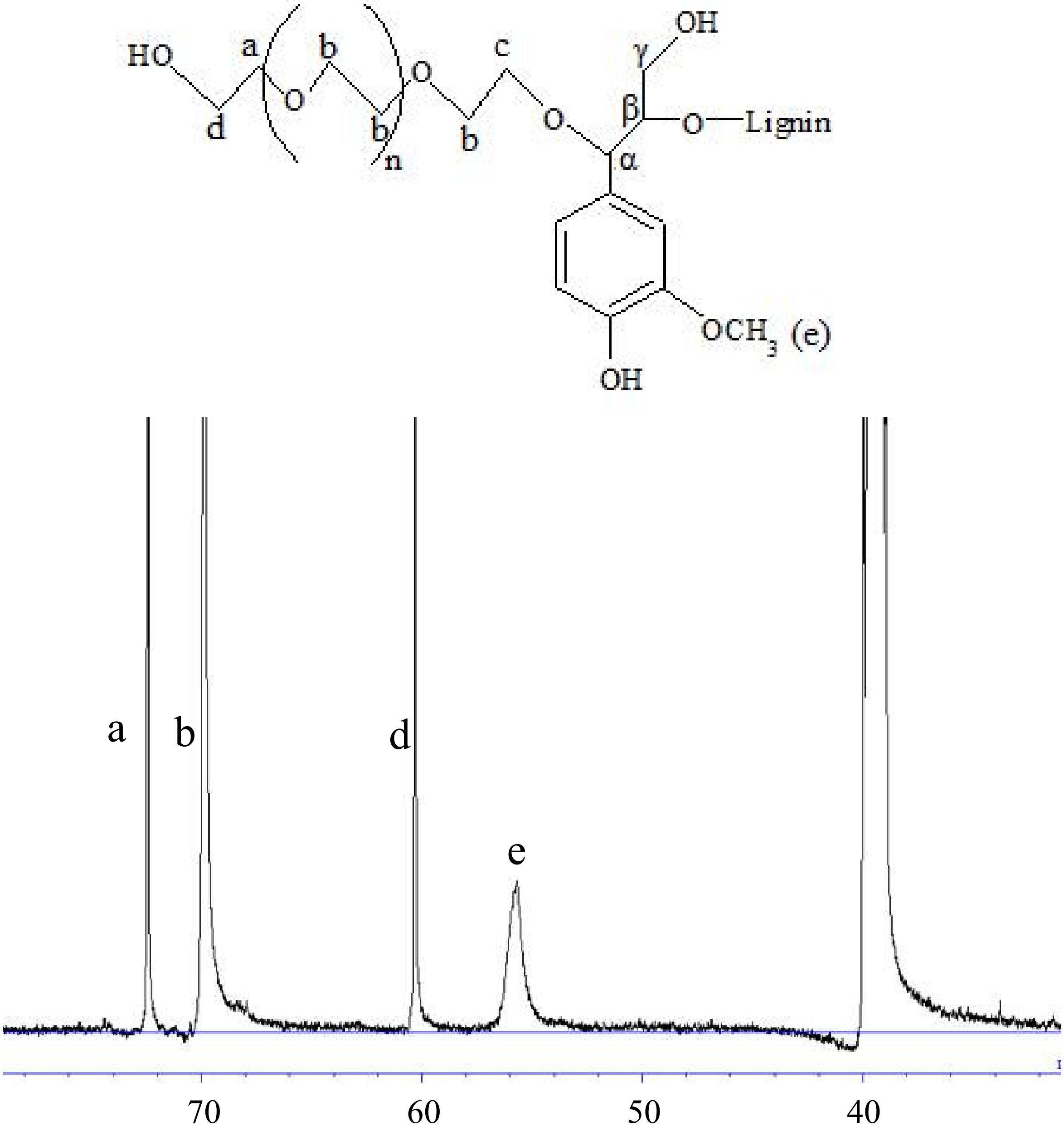


Figure 29. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 400

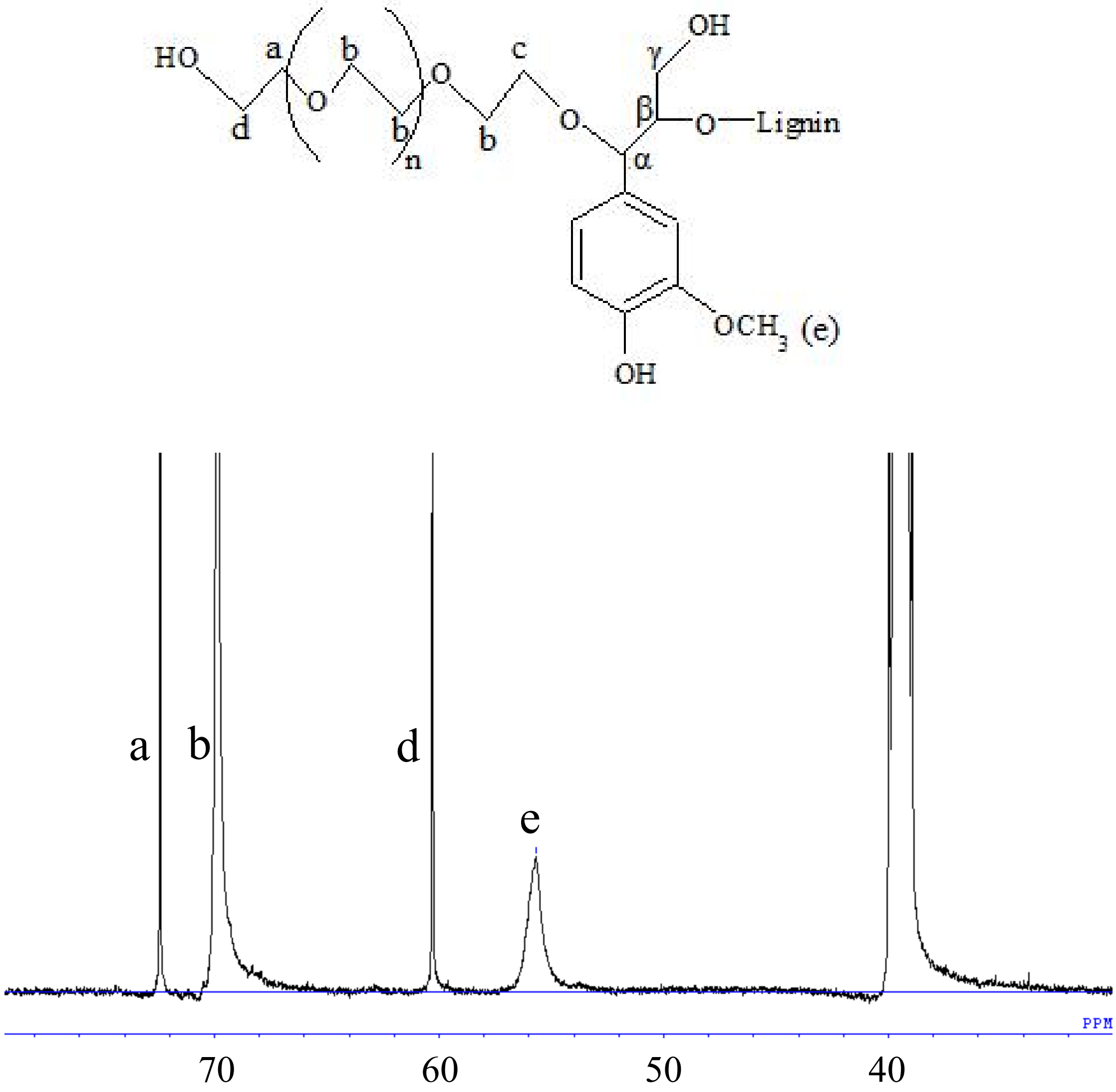


Figure 30. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin with PEG 1000

3-4 Effect of the reaction time of alkaline PEG treatment on grafting PEG onto lignin

Figure 31 shows a proposed reaction mechanism of the soda lignin in the alkaline PEG treatment. In the alkaline PEG treatment, the alkaline PEG-treated lignin (a) can be converted into intermediate of the quinone methide type (b) by adding an electron produced from free phenolic hydroxyl groups in different lignin units. (b) structure and a cycolhexadienone anion (c) of lignin by resonance canbe a diphenyl type structure (d), which is condensed by addition reaction. (d) structure can be an addition product (e) with rearomatization. Then, (e) structure can be a carbanion structure (e) by addition of proton. I think that (e) structure increase with increasing reaction time in the alkaline PEG treatment. Because, the step from (d) to (f) is irreversible reaction step. Finally, the alkaline PEG-treated lignin may be eliminated by increasing the carbanion structure with reaction time, as shown Fig. 31.

Figure 32 shows effect of the reaction time on the lignin content of the alkaline PEG-treated lignin prepared from purified lignin. The lignin content of the alkaline PEG-treated lignin prepared from the purified lignin for 60 minutes was the lowest sample in the alkaline PEG-treated lignin for variouse reaction time. This indicated that a high amount of PEG was introduced into the lignin when the grafting reaction time was performed for 60 minutes.

Figure 33 shows ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin for 60 minutes. The three signals (a, b, and d) could be detected in this NMR data. On the other hand, the signal (c) was not detected in this spectra of the alkaline PEG-treated lignin prepared from purified lignin for 60 minutes. This data suggested that there was no linkage between lignin and PEG on the alkaline PEG-treated lignin prepared from purified lignin for 60 minutes.

The most amount of PEG was introduced into the purified lignin when the grafting reaction time was performed for 60 minutes. However, it was difficult to confirm the reaction site between lignin and PEG on the alkaline PEG-treated lignin prepared from purified lignin. A high amount of PEG in the alkaline PEG-treated lignin performed for positive reaction time such as 60 minutes might have no influence on the reaction site between purified lignin and PEG.

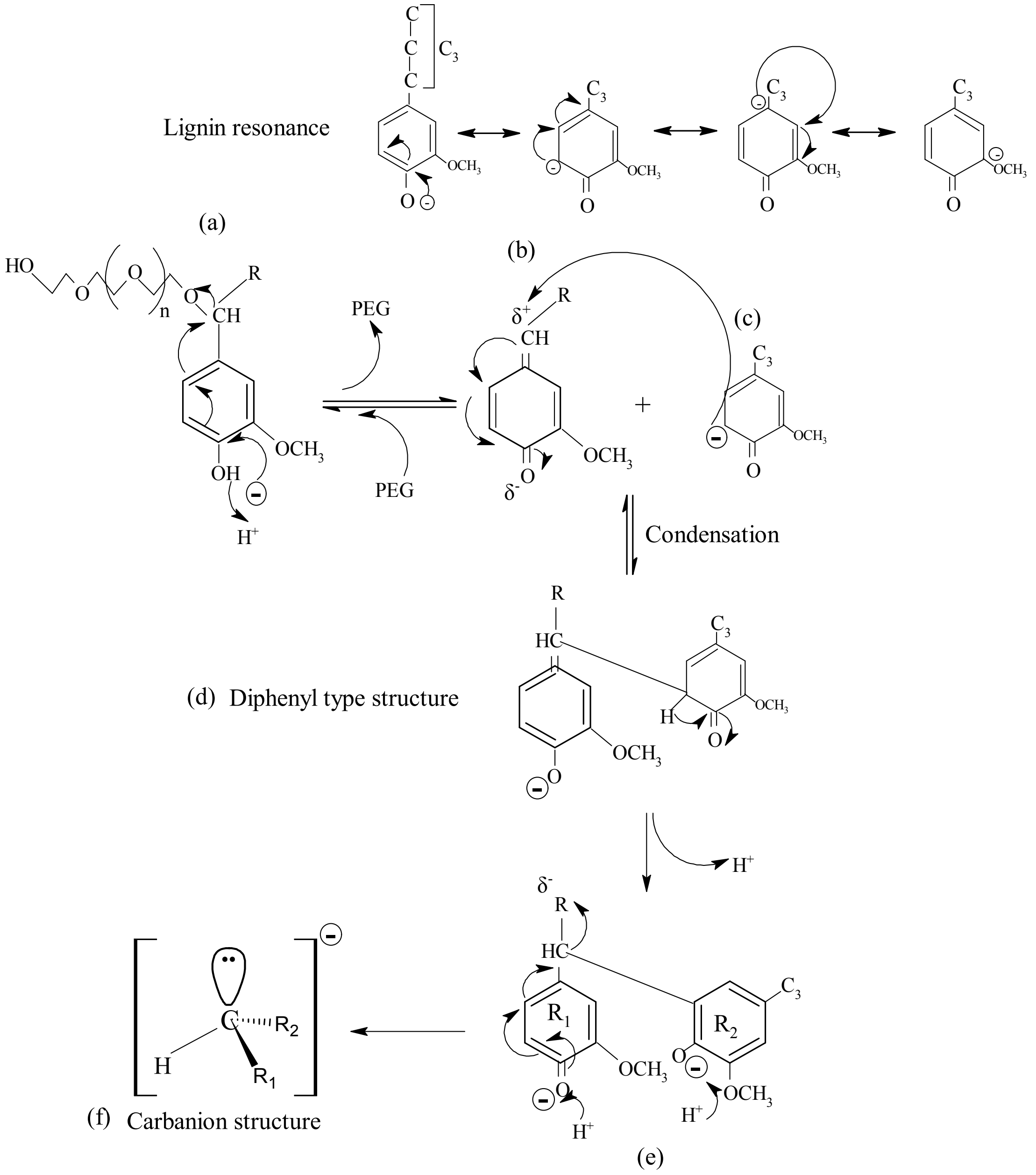


Figure 31. A reaction mechanism of alkaline PEG treatment

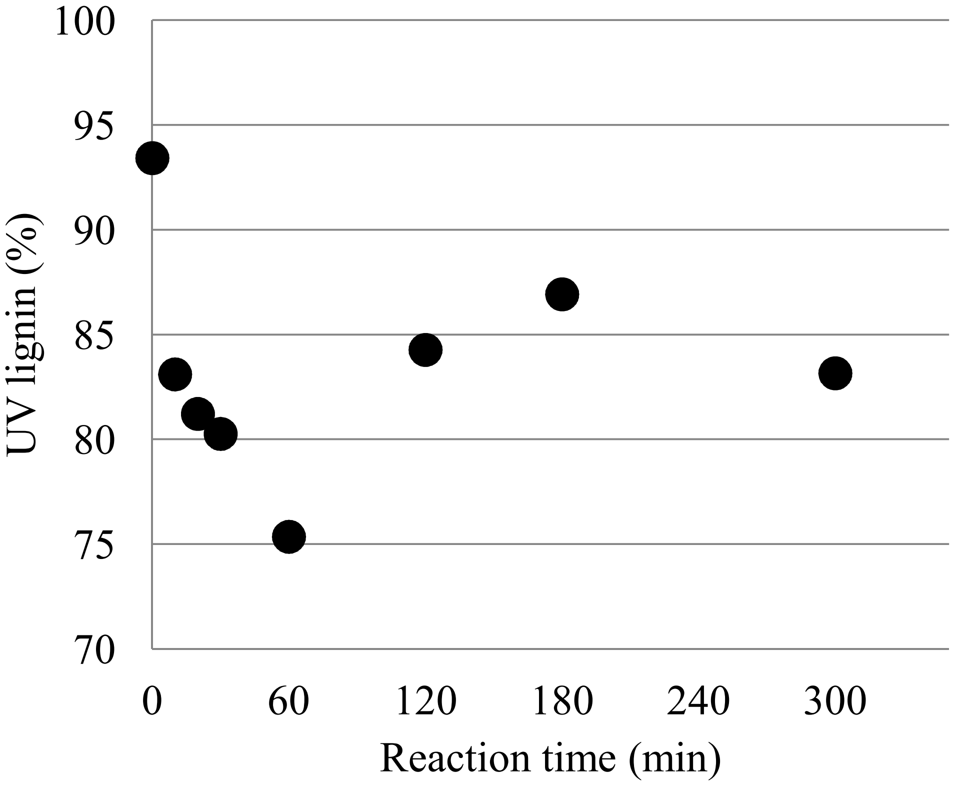


Figure 32. Effect of the reaction time on the lignin content of the alkaline PEG-treated lignin prepared from purified lignin

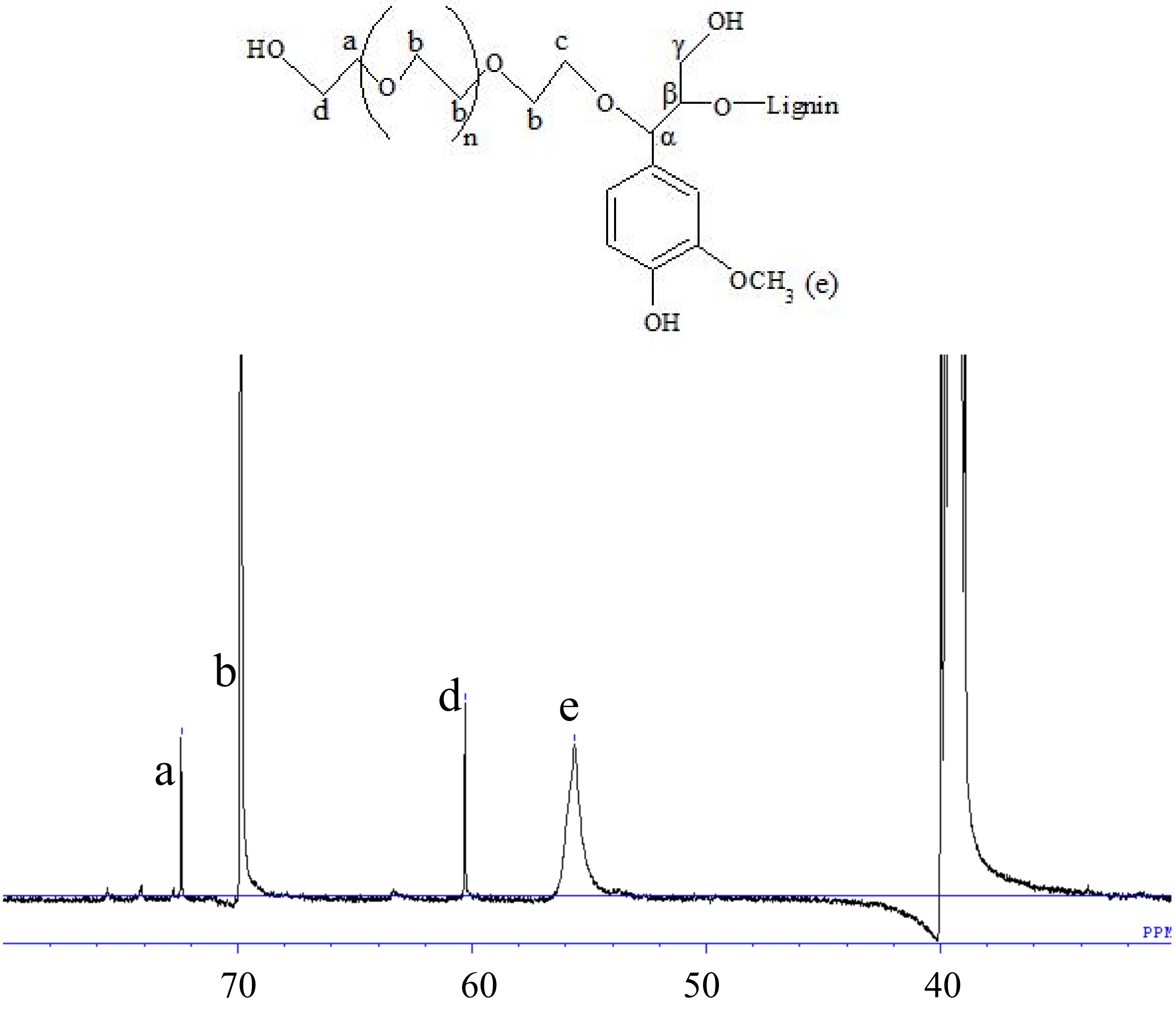


Figure 33. ^{13}C－NMR spectrum of alkaline PEG-treated lignin prepared from purified lignin (Reaction time : 60 min)

3-5 Reaction of acid-soluble lignin

The alkaline PEG-treated lignin prepared from black liquor powder exhibited thermal melting properties. However, the alkaline PEG-treated lignin prepared from purified lignin showed weak thermal melting during softening point analysis and did not show appropriate thermal melting performance during TMA analysis. Black liquor powder includes a considerable amount of lignin and consists of acid-insoluble lignin (62 %) and acid-soluble lignin (38 %), as shown in Figure 34. As the lignin in black liquor powder includes both acid-insoluble lignin (purified lignin) and acid-soluble lignin, alkaline PEG treatment was performed using the acid-soluble lignin as a model compound. A preparation procedure of acid-soluble lignin was shown in Figure 35. It was extraction from an acid-soluble fraction in the black liquor powder by acidifying.

Figure 36 shows the ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from acid-soluble fraction using EG. In this NMR data, the three signals (a, b, and d) could also be detected. In addition, a small signal 65.8 ppm (c) was detected. However, this NMR spectrum was difficult to determine the relationship between the acid-soluble lignin and PEG in the alkaline PEG treatment. Because, the signal (c) in the Fig.36 was detected with unknown signals in this NMR spectrum. It could be thought that the unknown signals indicated residue of carbohydrates due to lack of purification in the extraction of acid-soluble lignin. After purifying the acid soluble fraction by repeating a chloroform extraction step, the acid-soluble lignin was used in the alkaline PEG treatment as a model experiment.

Figure 37 shows the ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from the acid-soluble lignin fraction. This alkaline PEG-treated lignin was prepared in the PEG 1000 series. The signal (e) at 55.4 ppm was assigned to the carbon atoms of lignin methoxy groups. The strong signal at 69.8 ppm (Fig. 37b) was assigned to the methylene carbons of the repeating unit of the PEG polymer. The signals at 72.4 ppm (Fig.37a) and 60.3 ppm (Fig. 37d) were assigned to the methylene carbons of the alcohol end-groups of PEG. In addition, a strong signal at 66.4 ppm (Fig. 37c) was detected. The signal was assigned to methylene carbons bonded to the α-carbon on the lignin side chain *via* an ether linkage (Kishimoto *et al.* 2004). This spectrum strongly suggests that PEG was introduced to acid-soluble lignin at its α-carbon position. In the spectrum of the alkaline PEG-treated lignin prepared from black liquor powder (Fig. 17), the small signal (c) might be caused by the reaction of the acid-soluble lignin in the black liquor powder. The alkaline PEG-treated lignin prepared from black liquor powder exhibited good thermal melting properties. However, the alkaline PEG-treated lignin prepared from purified lignin exhibited week thermal melting properties and did not exhibit appropriate thermal melting performance during TMA analysis. The acid-soluble lignin in black liquor powder could provide thermal melting characteristics to the alkaline PEG-treated lignin prepared from black liquor powder. The data shown in Fig. 37 suggests that the acid-soluble lignin reacted with PEG to produce PEG-lignin derivatives. These derivatives may work as a plasticizer to induce the thermal melting of alkaline PEG-treated lignin prepared from black liquor powder.

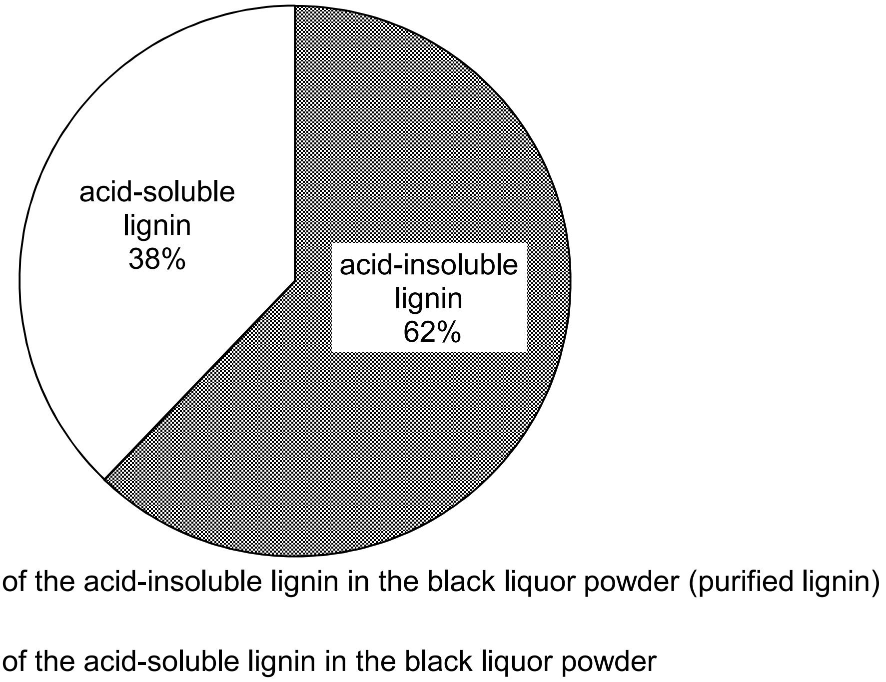


Figure 34. Percentage of acid-soluble and acid-insoluble lignin in black liquor powder

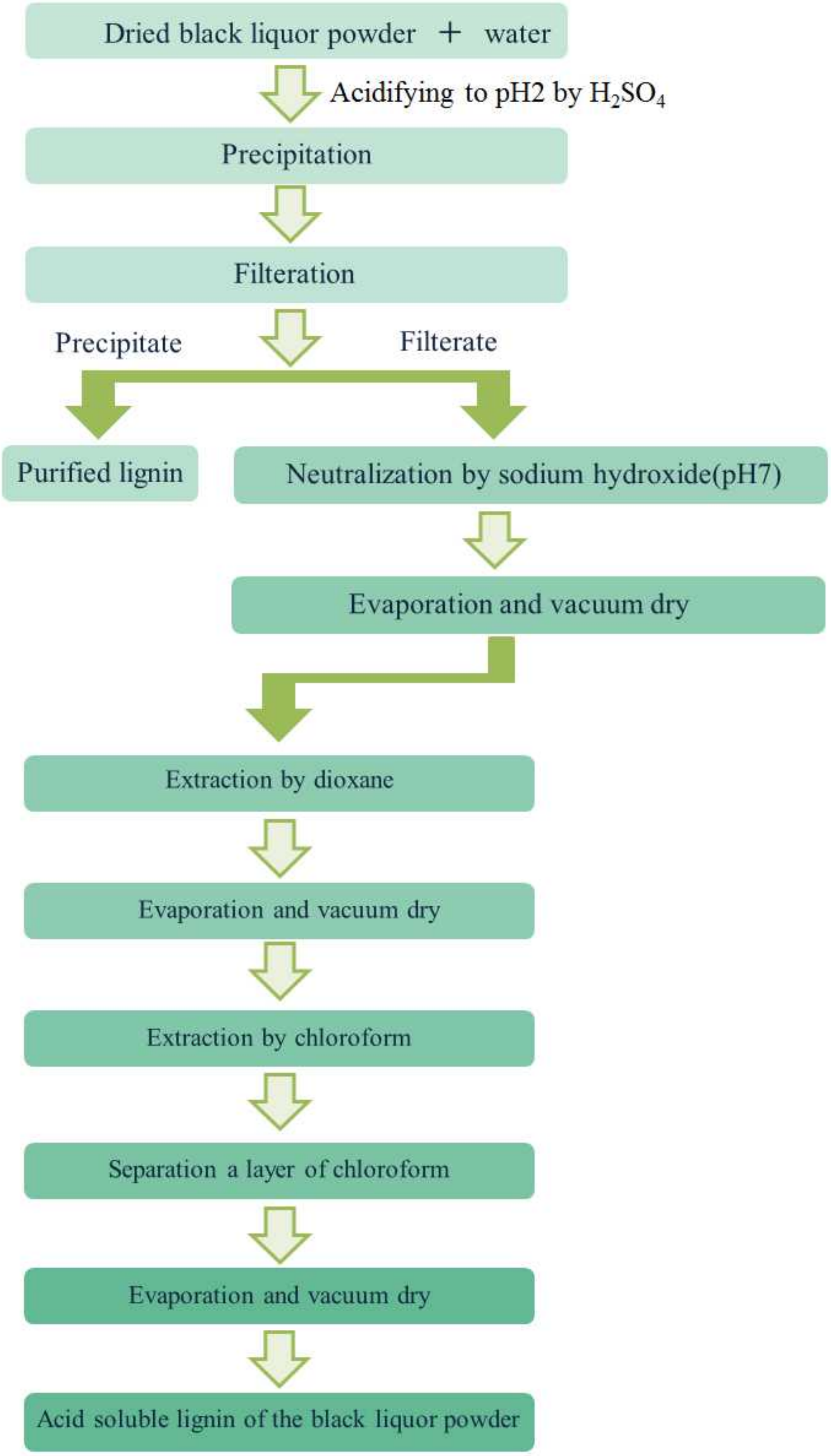


Figure 35. Preparation scheme for acid-soluble lignin of black liquor powder

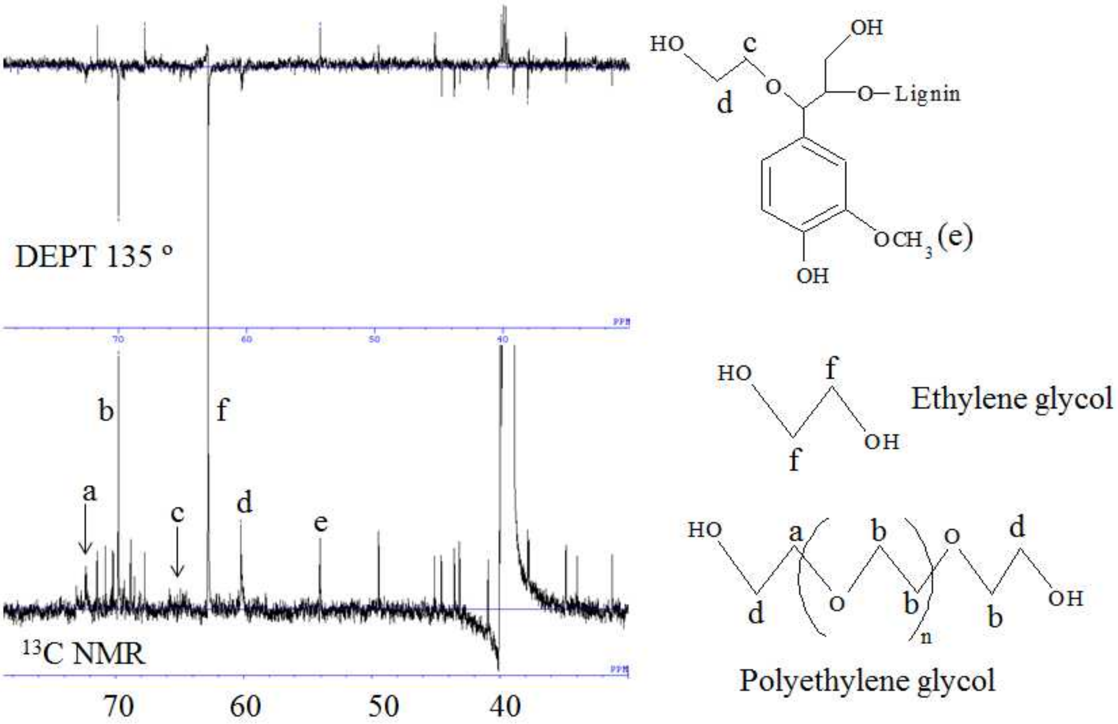


Figure 36. ^{13}C−NMR spectrum of alkaline PEG-treated lignin prepared from acid-soluble lignin fraction using EG

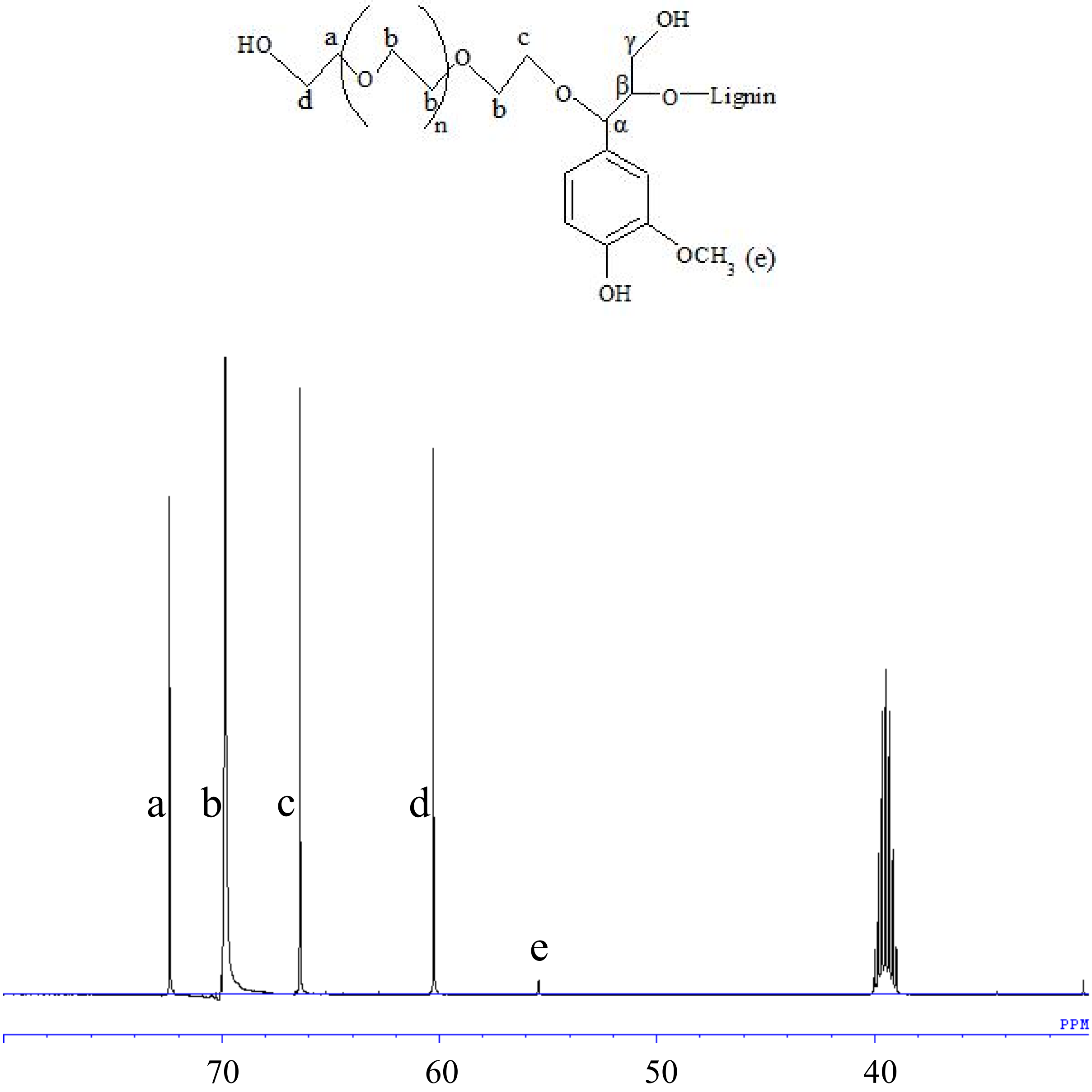


Figure 37. ^{13}C—NMR spectrum of alkaline PEG-treated lignin prepared from acid-soluble lignin fraction using PEG 1000

4 Conclusion

1. Alkaline PEG-treated lignin prepared from black liquor powder exhibited good thermal melting properties; on the other hand, that prepared from purified lignin exhibited weak thermal melting during softening point analysis and did not exhibit appropriate thermal melting during TMA analysis.

2. The lignin in black liquor powder includes both acid-insoluble lignin (purified lignin) and acid-soluble lignin. The NMR data of the alkaline PEG-treated lignin prepared from purified lignin suggest that there was no linkage between lignin and PEG in the samples. On the other hand, the NMR data of samples prepared from the acid-soluble lignin fraction suggest that PEG was grafted onto the lignin, thus producing PEG-lignin derivatives. PEG-lignin derivatives may work as a plasticizer to induce the thermal melting of alkaline PEG-treated lignin prepared from black liquor powder.

Chapter 5 General conclusions

In this study, a simple method for lignin derivatization using a spray-dried black liquor powder as a starting material was applied to the process of lignin modification from softwood.

Chapter 2 explains a process for the preparation of a black liquor powder from black liquor.

The results were as follows:

The material in this study was prepared from black liquor, which was dried to a powder using a spray dryer system. The total lignin content of each raw material (black liquor powder and purified lignin) used in this study is equal to the sum of their contents of acid-soluble lignin derived from the Klason method and the acid-insoluble lignin (Klason lignin). The total lignin content of the black liquor powder was 19.2% (w/w) and that of the purified lignin was 97.7% (w/w). The ABS coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration and UV absorbance of purified lignin at 280 nm. The ABS coefficient was 26.1 $L \cdot g^{-1} \cdot cm^{-1}$. The black liquor powder consisted of sodium hydroxide (7.3%, w/w), sodium carbonate (66.7%, w/w), and lignin (18.0%, w/w).

Chapter 3 presents experiments on the treatment of lignin derived from black liquor powder with alkaline PEG, and the chemical and thermal characteristics of the derivatized lignin.

The results were as follows:

1. The alkaline PEG-treated lignin from a softwood soda-AQ black liquor powder showed thermal melting characteristics with heating.

2. After alkaline PEG treatment at 120 °C , the samples treated with PEG 1000 and PEG 2000 showed thermal melting; however, the samples using PEG of lower molecular weights (*i.e.*, 600, 400, and 200) did not exhibit significant thermal melting. On the other hand, after alkaline PEG treatment at 160 °C, all samples showed thermal melting.

3. The treatment temperature and molecular weight of PEG had considerable effects on the physical properties of the alkaline PEG-treated lignin. The better melting characteristics of the lignin treated with PEG at 160 °C could be due to the higher amount of PEG grafted onto the soda-AQ lignin. The NMR data suggested that the PEG grafted to the α-carbon of lignin *via* an ether linkage.

Chapter 4 presents model experiments to clarify the reaction of softwood lignin in the alkaline PEG treatment using a purified lignin and an acid-soluble lignin.

The results were as follows:

1. Alkaline PEG-treated lignin prepared from black liquor powder exhibited good thermal melting properties; on the other hand, that prepared from purified lignin exhibited weak thermal melting during softening point analysis and did not exhibit appropriate thermal melting during TMA analysis.

2. The lignin in black liquor powder includes both acid-insoluble lignin (purified lignin) and acid-soluble lignin. The NMR data of the alkaline PEG-treated lignin prepared from purified lignin suggest that there was no linkage between lignin and PEG in the samples. On the other hand, the NMR data of samples prepared from the acid-soluble lignin fraction suggest that PEG was grafted onto the lignin, thus producing PEG-lignin derivatives. PEG-lignin derivatives may work as plasticizers to induce the thermal melting of alkaline PEG-treated lignin prepared from black liquor powder.

From the above, this thesis provides knowledge about the production of lignin derivatives by alkaline PEG treatment, which may facilitate the development of new technologies for the material utilization of lignin, which is a major component of woody biomass. It was shown that lignin derivatives could be obtained by a simple softwood lignin modification method using a spray-dried black liquor powder as a starting material. The black liquor powder was dissolved into PEG solution and heated at atmospheric pressure. After the reaction, the alkaline PEG-treated lignin was precipitated with acid and recovered by filtration. The lignin derivatives showed adequate thermal melting characteristics for conversion to a lignin material with a thermal melting property. This thesis demonstrates a process for producing high value-added products from lignin in the black liquor, which until now has been discharged as a byproduct of pulp.

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