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THE THESIS FOR THE DEGREE OF MASTER SCIENCE

Study on the Precipitation Behavior of Lignin in Black Liquor Using Iron (III) Chloride

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Abstract

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In kraft pulping industry, the huge amount of kraft lignin has been produced every year and converted to heat energy for steam and electricity by evaporating black liquor and burning it in furnace. To valorize kraft lignin, isolation of lignin from black liquor is required. However, acid precipitation method which has been used conventionally uses strong acid and it occurs several problems such as facility corrosion. Therefore, lignin precipitation methods which do not use strong acid have been needed to solve these problems.

In this study, precipitation of lignin in black liquor was conducted by using metal salts because it can precipitate lignin in alkali condition. To analyze the mechanism of precipitation, raw black liquor, acid precipitated lignin and dialyzed kraft lignin were used. As a precipitator, iron chloride was used. Different dosage of iron chloride solutions were prepared in different ratio of ethanol and deionized water (ethanol:deionized water = 100:0, 75:25, 50:50, 25:75, 0:100). After then, each lignin solution was put into iron chloride solution (volume ratio of iron chloride solution/liquor = 0.5) and stirred at 150
rpm for 30 min. After 1 h, mixture was centrifuged and freeze-dried. The iron chloride solutions (ethanol, deionized water solvent) were analyzed by using ultraviolet-visible spectroscopy to figure out Fe species in solution. Precipitated solid was analyzed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and gel permeation chromatography (GPC) to figure out precipitation mechanism.

Fresh black liquor was used to analyze the behavior of precipitation. Different input of iron chloride (0.5, 1.0, 1.5, 3.0, 4.0 % (w/v)) solutions were prepared in only ethanol solvent. The 100 ml of raw black liquor was put into iron chloride solution (volume of iron chloride solution = 10, 33, 50, 100 ml). The mixture was stirred at 150 rpm for 30 min. After 1 h, mixture was centrifuged and freeze-dried. The removal of solid and kraft lignin in black liquor were calculated. The precipitation temperature was set at room temperature and 65°C.

In this study, iron chloride and kraft lignin only showed sweep flocculation by Fe sludge which was formed by metal polymerization. The critical coagulation concentration which is feature of zeta-potential neutralization was not observed. When iron chloride was dissolved in deionized water as a solvent, removal of solid in black liquor was not affected by input of iron chloride. In contrast, in ethanol solvent, solid in black liquor was precipitated and weight of precipitate increased in proportion to input of iron chloride. This is because lignin could be polydentate ligand of Fe species and hinder metal polymerization by blocking growth site of Fe species. However, ethanol could prevent binding of lignin and assist formation of sludge.

In sweep flocculation, solvent of iron chloride, properties of lignin and ions in black liquor were considered as important factors. According to UV-visible spectroscopy, iron chloride showed high concentration of free ferric ion which is favorable speices in metal polymerization at ethanol solvent, but most
of the Fe species had hydroxide forms in water solvent (solvent effect). When highly soluble lignin was present in liquor, formation of sludge and Fe-lignin insoluble particle was hindered. However, when highly soluble lignin (such as lignin carbohydrate complex (LCC)) was removed by acid precipitation process, precipitation of lignin in black liquor occurred even in water solvent contrary to raw black liquor. This is because formation of sludge and Fe-lignin insoluble particle was activated by removing highly soluble lignin in liquor. According to GPC analysis, most of the high molecular weight lignin was precipitated, whereas low molecular weight lignin was not precipitated (lignin effect). Cations in black liquor also affected sweep flocculation. When the concentration of ion was very low, dialyzed lignin solution showed very poor lignin removal. However, dialyzed lignin solution with sodium chloride showed significant increase in removal of lignin compared with dialyzed lignin solution with no cations (ionic effect).

Black liquor and iron chloride showed the highest removal of solid and lignin in black liquor when the volume ratio of ethanol solvent and black liquor was 0.1. This was because the concentration of ferric ion for metal polymerization was high. Removal of solid and lignin in black liquor increased in proportion to input of iron chloride, but increase of precipitation after 3.0% (w/v) of iron chloride was very small. Temperature of black liquor did not show any effect in precipitation.

Key words: kraft lignin, precipitation, iron chloride, sweep flocculation, sludge, metal polymerization

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1. Introduction

1.1. Lignin structures & kraft lignin

Lignin is natural organic polymer that occupies 20-35% weight percent of plants and takes up the second largest amount in natural polymer following cellulose. From biomass industry, lignin is obtained over 72 million tons per year (Li et al., 2015).

Lignin has cross-linked structure of hydroxyl-phenylpropane units called monolignol such as \( p \)-coumaryl (H type), coniferyl (G type) and sinapyl (S type) alcohols. The cross-linkages consist of ether (C-O-C) and carbon-carbon (C-C) linkages. The ether linkages are mainly composed of \( \beta \)-O-4, \( \alpha \)-O-4 and 4-O-5 (Sjöström, 1993). In the case of carbon-carbon linkages, 5-5, \( \beta \)-5, \( \beta \)-1 and \( \beta \)-\( \beta \) structures are predominant forms. The complex cross-linked structure of lignin is one of the major factors for heterogeneous property of lignin and makes lignin hard to be utilized. However, in several chemical biomass industries such as pulping, various researches on the lignin utilization have been conducted recently due to potential for being a high-value material. For instance, many studies refer that lignin has a variety of beneficial properties such as metal cation removal properties (Lalvani et al., 1997), anti-oxidant property (Pouteau et al., 2003), bio-degradable property (Richter et al., 2016). Therefore, in order to utilize lignin as a high value material, proper and cost-efficient lignin isolation and purification processes are required (Cui et al., 2014).

Among the biomass industries, most of the lignin production comes from kraft pulping and that lignin is called kraft lignin. The amount of lignin from kraft pulping accounts for 85% of total technical lignin production around the world (He & Fatehi, 2015). In kraft pulping industry, the lignin is obtained
from wood chips put into digester with “white liquor” (Zhu, 2015). White liquor which is composed of sodium hydroxide and sodium sulfide makes lignin dissolved in the liquor under elevated temperature condition (cooking process) (Chakar & Ragauskas, 2004; Norgren et al., 2001). During the cooking process, white liquor usually cleaves α-aryl and β-aryl ether linkage of lignin via quinone methide intermediate. This degradation reaction is shown in Figure 1 (Chakar & Ragauskas, 2004). Because of the cleavage of ether linkage, kraft lignin has a lot of phenolic hydroxyl groups (Sadeghifar et al., 2012). In alkaline condition, phenolic hydroxyl groups are ionized and increase hydrophilicity of lignin. As a result, lignin is depolymerized and forms alkaline solution called “black liquor”.
Cleavage of $\alpha$-aryl ether linkage in lignin during cooking process

Cleavage of $\beta$-aryl ether linkage in lignin during cooking process

Figure 1. Lignin degradation mechanism during kraft pulping process. (a) is cleavage of $\alpha$-aryl ether linkage in lignin and (b) is cleavage of $\beta$-aryl ether linkage in lignin (Chakar & Ragauskas, 2004).
1.2. Conventional black liquor treatment process in kraft pulping

Kraft pulping is the most predominant method in pulping industry (Gellerstedt et al., 2004). In kraft pulping, lignin in black liquor has been conventionally used as steam and power sources of plant. Every ton of pulp produces about 10 tons of black liquor and over 1.3 billion tons of black liquor are processed per year (Tran & Vakkilainnen, 2008). In kraft pulping, the black liquor is usually treated by several processes to recover white liquor for recycling of chemicals. For this reason, lignin needs to be separated from the liquor, which has been achieved by “white liquor recovery process” which is burning lignin. Rest of chemicals are regenerated to white liquor by “causticizing process” which converts sodium carbonate to sodium hydroxide (Biermann, 1996). The entire scheme of the process is shown in Figure. 2 (Tran & Vakkilainnen, 2008).

In order to burn the lignin in black liquor, increase of solid content of the liquor is needed because high moisture content can be an obstacle in burning process. For this reason, black liquor goes to evaporator first and is typically concentrated to 65% or higher solid content by evaporating. This concentrated black liquor is called as “strong black liquor”, which is burned in recovery boiler. By burning process, lignin, polysaccharides and some extractives are combusted and sufficient power for steam and electricity is obtained from the heat (Chen et al., 2014).

However, it is not easy to handling black liquor because plants have experienced several bottlenecks in their conventional black liquor treatment process. Among several problems, the most critical one is process problems which are caused during evaporating such as tube corrosion, foaming and high steam consumption (Tran & Vakkilainnen, 2008). In terms of process problem, one of the most important factors of bottlenecks is high liquor viscosity caused
by lignin (Hill et al., 1988). According to previous studies, black liquor typically contains about 30 ~ 34% of the lignin and the viscosity of the liquor is getting higher and higher as the cooking and recovery processes are progressed. Besides, 2 ~ 3% of polysaccharides in liquor also contribute to increasing liquor viscosity (Roberts et al., 1996). High liquor viscosity with high molecular weight of lignin makes muti-effect evaporator require much more energy by leading liquor to poor heat circulation and low heat transfer coefficients.
Figure 2. Scheme of black liquor treatment process (Tran & Vakkilainen, 2008)
1.3. Concept and needs of precipitation

To solve problems in conventional black liquor treatment process, several methods have been tried. Among them, precipitation and isolation of kraft lignin in black liquor can be promising method because most of the problems are from high liquor viscosity caused by lignin in black liquor.

As precipitation method, the acid precipitation have been used predominantly (Gilarranz et al., 1998). Lignin in black liquor has a lot of free hydroxyl group in its structures and they are deprotonated in alkali condition (Sadeghifar et al., 2012). Because white and black liquor are strong alkali condition, lignin can have hydrophilicity and be dissolved in liquor. However, when liquor’s pH decreases by adding acid, free hydroxyl and phenolic hydroxyl group obtain protons. Thus, lignin loses its hydrophilicity and is precipitated.

As other precipitation methods, kraft lignin’s colloidal properties also can be used. According to several studies, kraft lignin have negative zeta-potential and is dispersed by repulsive force between particles (Lindströmmn, 1979). However, this repulsive force can be removed through charge neutralization and big flocs can be made by adding cationic coagulants. In addition to charge neutralization, kraft lignin particle can be precipitated by “sweep flocculation” using polycationic coagulants like ferric species. Metal salts like ferric chloride form huge polymeric structure in alkali condition by olation and oxolation and they make big flocs and are precipitated with kraft lignin particles (Jolivet et al., 2004).

Acid precipitation method have high yield and is easy to use. However, entire pulping process is under strong alkali condition and black liquor have to be recovered to white liquor to reuse. Thus, using strong acid can make critical problems in terms of cost efficiency and environment. In terms, precipitation
methods applying kraft lignin’s colloidal properties can be promising method because it can be done in alkali condition and this can be benefit. Therefore, research on kraft lignin’s colloidal properties and characteristic of coagulants in black liquor must be needed.
1.4. Objectives

Currently, kraft pulping industry has been faced with lignin handling problems because kraft lignin usually increases liquor’s viscosity and causes several process problems like tube corrosion. In addition, kraft lignin has been used as heat source which is low value material. To valorize kraft lignin and solve problems which are occurring in black liquor treatment process, many researchers have done and referred to precipitation of lignin as a possible solution.

In order to isolate kraft lignin from black liquor typically acid precipitation is used. However, acidifying black liquor which is strong alkali is very inefficient and can be severe problem in precipitation facility and environment. For this reason, only small portion of kraft lignin has been utilized as other materials and most of the lignin have been burned as fuel. Therefore, to utilize kraft lignin as high value materials, precipitation in alkali condition is necessary. According to the several studies, lignin in black liquor has colloidal properties and metal salts such as iron chloride can precipitate lignin in black liquor at alkali condition.

Specifically, the aims of this study are:
1. To elucidate precipitation mechanism of lignin in black liquor through interaction between lignin and iron chloride

2. To analyze effects of several factors such as temperature, solvents, dosage of iron chloride on precipitation behavior.

3. To evaluate removal of lignin and determine optimum condition for precipitation of lignin in black liquor using iron chloride
2. Literature reviews

2.1. Colloidal properties of kraft lignin

Kraft lignin in black liquor is not a simple organic compound and also not a simple solute. The lignin exists in solution as colloidal particle and that of properties vary along with their structures (Nyman et al., 1986). To elucidate colloidal properties of kraft lignin in black liquor, several studies have been conducted.

Lindström (1979) reported effects of dissociation degree of lignin in solution. It was described reduced viscosity along with dissociation degree by adding various amount of sodium hydroxide. The reduced viscosity decreased as the dissociation degree of kraft lignin increase. This result showed some different tendency compared with typical polyelectrolytes. In the case of regular polyelectrolites, the viscosity increases when degree of dissociation increases. Because protons in molecules are dissociated and transforming to long chain form by electrostatic repulsion force between fuctional groups. This phenomenon can be evidence that lignin is not a simple polyelectrolyte and has colloidal property. Lindström also mentioned about effect of storage. Intrinsic viscosity increased when degree of dissociation was 0 and elevated temperature (thermally irreversible). When degree of dissociation was over 0.2, intrinsic viscosity decreased. From these data, carboxylic acid and phenolic OH played important role in association between lignin particles by hydrogen bonding because high-pH (high degree of dissociation) makes carboxylic groups ionized and breaks aggregate already formed. In addition, thermally irreversible properties were accordacne with lyophobic colloid properties. (Lindström, 1979)
Lappan et al. (1997) conducted some experiments to understand colloidal properties and interaction between kraft lignin and polycation. The study reported that poly (DADMAC) can precipitate kraft lignin from 80 ~ 90% at pH 10 ~ 12.5 and the requirement dosage of polycation increased at high pH of solution because kraft lignin and poly (DADMAC) was more ionized in high pH. However, only small amount of the poly (DADMAC) was in precipitated lignin and the precipitated lignin was not fully neutralized. To elucidate this phenomenon, the research proposed that most of poly (DADMAC) were combined with more hydrophilic and amphipathic lignin-carbohydrate polymers which cannot be precipitated. This is because kraft lignin / poly (DADMAC) floc formation follows the models which is assumed that primary particles are formed rapidly and after that they undergo diffusion-controlled coagulation. In terms of this work, the lignin in black liquor could have several structures and make lignin have different colloidal properties (Lappan et al., 1997).

2.2. Principles of precipitation by metal salts

To analyze colloidal properties and precipitation of kraft lignin, understanding principle of coagulation is very important. The mechanisms of coagulation by metal salts are not fully explained yet. However, some researchers did several studies and announced reasonable mechanisms. Among many metal salts, the following is mainly about iron and aluminum.

Oriekhova & Stoll (2014) tried to elucidate coagulation mechanism of FeCl₃ hexahydrates in latex solution. The study mentioned that iron had free cation and several hydroxide forms depending on the initial pH of solution and played a role of surface neutralizer. Cationic iron ion made zeta-potential of latex particles closer to zero and precipitated because electrostatic repulsion
force was removed. When pH of solution was high, latex appeared high-negative zeta potential and required more coagulant. In contrary, when pH of solution was low, latex had low-negative zeta potential and required less coagulant. In addition to pH, dosage also influenced coagulation. Excessive dosage of iron chloride reversed zeta potential and re-stabilized latex particles in solution. To achieve effective coagulation, the study stated that pH and optimum dosage must be considered (Oriekhova & Stoll, 2014a).

Duan and Gregory, (2003) reviewed two major mechanisms of coagulation by metal salts. One is surface neutralization and the other is sweep flocculation. The former is that metal salts are hydrolyzed in solution and positive charged hydrolysates adsorb on particles. The adsorption of metal cation removed electrostatic repulsion force of particles and the particles were precipitated. The hydrolyzed metal salts, especially, make inner surface complexes and combine much stronger than free metal ion. The latter is quite different with surface neutralization. When metal salts were overdosage, particles made more large flocs and much fast precipitation occurred. This phenomenon could not make sense because overdosage usually causes zeta-potential reverse and re-stabilization of particle. However, after the re-stabilization, more dosage of metal salts made metal salts form big sludge which covered impurity particles and this sludge made particles be precipitated. The evidence was that the large flocs were irreversible for floc break and solution showed twice of turbidity drop as metal salts were added. The first turbidity drop was surface neutralization and the second was sweep flocculation. Although sweep flocculation is considered as one of the major factors of metal salt precipitation, the exact explanation about sweep flocculation is not yet proposed (Duan & Gregory, 2003).

Kraft lignin has lyophobic colloidal properties which are susceptible to coagulant and metal salt can be coagulants by surface neutralization and sweep flocculation (Norgren & Edlund, 2003). About this topic, Lindstrom and
Sundin researched on metal salts coagulation of kraft lignin.

Lindstrom conducted several experiments using monovalent, divalent and multivalent metal salts. Lindstrom referred that critical coagulation concentration (CCC) which means minimum dosage to occur precipitation was significantly different depending on type of metals, pH, and temperature. The study referred monovalent metals required different order of coagulant. For example, LiCl required more than one hundred times of coagulants than MgCl₂. In addition, monovalent metals were not affected by temperature and monovalent and divalent metals were not affected by lignin concentration. However, divalent and multivalent metals were affected by temperature. When temperature was relatively high, the CCC was significantly reduced. This is because the steric rearrangement could occur in flocs and mobility of particles was fast at high temperature. The research also mentioned the lignin concentration only affected multivalent metal salts. In contrary to other parameters, pH had the same tendency in all three types of metals. When the pH was getting higher, the CCC also increased. Because degree of dissociation of lignin could be increase in high pH, negative charge of lignin also could be increase and require much higher cation concentration. (Lindstrom, 1980)

Sundin, (2000) conducted research on lignin precipitation by metal ions in alkaline condition to applicate in brown stock washing during kraft pulping. Mainly used metal ions were Na⁺, Ca²⁺ and Mg²⁺. The Na⁺ could not precipitate lignin at high pH 12, 13, but only at high temperature and pH 11. In the case of Ca²⁺, using only small amount of Ca²⁺ could precipitate lignin even at high pH 9 ~ 13. This result was correspond to study conducted by Lindstrom. However, in the contrary to Lindstrom, Sundin referred Mg²⁺ had the smallest CCC at pH 11 not at pH 9. He insisted that isoelectric point of Mg²⁺ is above pH 12. In other words, it had positive charge at pH 11 and could be effective coagulants. Sundin also mentioned about precipitated lignin. From the study, the molecular weight of precipitated lignin using Ca²⁺ had above 1000 Daltons
and lignin which have less than 1000 Daltons did not have CCC (Sundin, 2000).

2.3. Characteristic of Fe species in solution

Currently, Fe salts have been widely used as metal salts coagulant in water treatment process. However, it has quite different properties with monovalent or divalent metals in solution. In addition, Fe is also affected by several factors and has different structures along with solution condition such as pH, kinds of organic solute in solution. To apply Fe salts to black liquor treatment process, the characteristic of Fe in solution must be understood. Although Fe complexes are so reactive that it is hard to elucidate the phenomena, there are several studies on Fe complex structure.

Jolivet, (2004) conducted several works on iron oxide chemistry and announced that the structural chemistry of iron ox(hydrox)ides was very rich and diverse. Fe usually had \[\text{Fe(OH)}_{6-4h}\text{H}_{6-h}\] form depending on solution pH. As the pH increases, hydroxyl ligand also increases and the polarity of Fe complexes was reduced. In addition, condensation of aquohydroxo and oxohydroxo complexes was proceeded by olation and oxolation. Olation is formation of hydroxo bridge between metal centers with dehydration and oxolation is formation of oxobridges between metal centers. More detailed mechanism was described in Figure 3. Julivet described that through these condensation reaction in base, Fe had crystallization structure and could make big particles which are important in nature system (Jolivet et al., 2004).

Davis & Edwards, (2017) conducted studies on precipitation of natural organic matter (NOM) using FeCl₃. Davis referred that adsorption of organic compound to Fe hydrolysate (iron hydroxide) made flocs which were key of removal of organic compounds from solution. In other words, Fe must be
hydrolyzed. However, Davis announced that NOM which has phenolic and carboxylic functional groups could be an obstacle to Fe hydrolysis because hydroxyl group competed with NOM to bind with Fe coordination sites. As a result, high concentration of NOM decreased hydrolysis ratio and NOM removal efficiency. However, Davis also referred that addition of Ca$^{2+}$ could improve hydrolysis ratio and removal efficiency even at high NOM concentration. Ca$^{2+}$ neutralized negative charge of NOM and minimized formation of NOM-Fe complex. Thus, Fe could be hydrolyzed and make flocs with NOM. In this aspect, Davis reported that calcium and concentration of NOM is very important factor in NOM removal. (Davis & Edwards, 2017)

Phenrat, (2008) conducted studies on arsenic compounds from water using FeCl$_3$. Phenrat referred that coagulation with ferric chloride is an effective and economical technique for removal arsenic compounds. Phenrat also reported that there were four major coagulation mechanism. 1) the formation and precipitation of insoluble compounds 2) the incorporation of soluble arsenic species into growing iron hydroxide phase. 3) the entrapment of adsorbed arsenic species in the interior of the growing iron hydroxide phase. 4) the binding of soluble arsenic to the external surfaces of the insoluble iron hydroxide. By using SEM-EDS, FT-IR and XRD, Phenrat showed that arsenic compounds follow mechanisms which are mentioned above. (Phenrat et al., 2008).
Figure 3. Mechanism of Fe condensation reaction and influence of pH. (a) and (b) are mechanisms of olation and oxolation. (c) is influence of pH on the solubility of iron crystal structure (Jolivet et al., 2004).
3. Materials and methods

3.1. Materials

Black liquor which was produced from kraft pulping process was used to precipitate kraft lignin and was provided from Moorim P&P Co., Ltd (Republic of Korea). Black liquor have two different solid content, strong black liquor and weak black liquor. Iron (III) chloride hexahydrate (97.0%) used as metal coagulant was purchased from SAMCHUN chemical (Pyeongtack, Republic of Korea). Ethanol (95.0%) used as solvent of iron (III) chloride hexahydrate was also purchased from SAMCHUN chemical. Sodium hydroxide (96%) was purchased from Junsei chemical Co., Ltd (Tokyo, Japan).

3.2. Chemical composition of black liquor

To analyze chemical composition of black liquor, solid, organic compounds and sugar content were measured. Solid content was measured by using oven drying method (105°C). Black liquor (5 g) was fully dried in 105°C oven for 24 h. After then, the solid from the black liquor was used to measure organic compound and sugar content. To analyze organic compound content, dried solid (0.2 g) was put on alumina crucible and burned in furnace for 3 h at 575°C. Sugar content was measured by using acid hydrolysis method. Dried solid (0.3 g) was reacted with 72% sulfuric acid for 1 h at 30°C and diluted with 84 ml of deionized water. Diluted samples were autoclaved for 1 h at 121°C and filtrated. The filtrate was analyzed using high performance liquid chromatography (HPLC; Ultimate 3000, Dionex, USA)
3.3. Precipitation of kraft lignin in black liquor

To analyze precipitation mechanism in black liquor using iron chloride, strong black liquor was used. Iron chloride was prepared in solution by using ethanol and deionized water as a solvent. The dosage of iron chloride was 1.5, 2.25, 3.0% (w/v) and prepared in 100 ml of solvent (ethanol:deionized water = 100:0, 75:25, 50:50, 25:75, 0:100). After that, 200 ml of strong black liquor was added to each iron chloride solution and stirred at 150 rpm for 30 min. After 1 h from adding black liquor, the solution was centrifuged to separate liquid and solid fraction. After then, the separated solid fraction was freeze-dried.

To analyze precipitation behavior of kraft lignin, fresh weak black liquor was used and precipitation process was conducted in several different condition such as different dosage of iron chloride hexahydrate, ratio of ethanol in solution and temperature. 100 ml of weak black liquor was put into several different iron chloride solutions which were prepared with following conditions. The dosage of iron chloride was 0.5, 1.0, 1.5, 3.0 and 4.0% (w/v). The solvent was ethanol (95%) and the volume was 10, 33, 50, 100 ml which were correspond to ethanol/black liquor volume ratio 1:10, 1:33, 1:2 and 1:1. Temperature was set at room temperature and 65℃. Higher temperature (65℃) was correspond to the temperature of weak black liquor which is at the end of digester of kraft pulping process and was maintained using oven. Mixed black liquor and iron chloride solution were stirred for 30 min at 150 rpm. After 1 h from black liquor was put, the solution was centrifuged to separate solid fraction from solvent and the solid fraction was freeze-dried.
3.4. Precipitation of treated kraft lignin in alkali solution

Two different treated kraft lignin was prepared to analyze precipitation mechanism in black liquor using iron chloride. One was acid precipitated kraft lignin and the other was dialyzed kraft lignin. After then, those of lignin was dissolved in alkali solution which had pH 12 to make similar condition with black liquor.

3.4.1. Precipitation of acid precipitated kraft lignin

Acid precipitated lignin was prepared by lowering pH of strong black liquor to pH 7 using 95% sulfuric acid. After solution pH was lowered, liquid and solid fraction were separated using centrifugation and the solid fraction was freeze-dried. After then, acid precipitated lignin was dissolved in deionized water with different concentration (5 and 10%, w/w) and pH was adjusted to 12 by using 1M NaOH solution. Iron chloride (1.5% (w/v)) was prepared in 35 ml of solvent (ethanol:deionized water = 100:0, 75:25, 50:50, 25:75, 0:100) and 70 ml of acid precipitated lignin liquor was put into iron chloride solution. The mixture was stirred at 150 rpm for 30 min. After 1 h from adding black liquor, the solution was centrifuged to separate liquid and solid fraction. The separated solid fraction was freeze-dried.

3.4.2. Precipitation of dialyzed kraft lignin

Dialyzed kraft lignin were prepared by dialysis membranes (H1, Cellu·Sep®, USA). Acid precipitated lignin was dissolved (5%, w/w) and adjusted by using 1M NaOH solution to pH 12. After that, kraft lignin solution was dialyzed for 48 h and deionized water which was used for dialysis was
changed frequently. After then, the dialyzed lignin solution was precipitated by using 95% sulfuric acid and freeze-dried. To make lignin solution, the dialyzed kraft lignin was dissolved in deionized water (3%, w/w). pH was adjusted to 12 by using 1M NaOH solution. Sodium chloride (1.5% (w/v)) was added in some of the samples to analyze effect of ions. Iron chloride (0.375 g) was prepared in 12.5 ml of solvent (ethanol:deionized water = 100:0 and 0:100) and 25 ml of dialyzed lignin liquor was put into iron chloride solution. After then, precipitated solid was obtained according to the same method above.

3.5. Characterization of iron chloride solution and precipitated lignin

3.5.1. Ultraviolet-visible spectroscopy

UV-visible spectrometer was used (UV-1601PC, SHIMADZU) to analyze effect of solvent in Fe solution. Fe solution was prepared in different solvent (deionized water and ethanol (95%)) and pH (2.5 and 3.5). pH was adjusted only in deionized water Fe solution by using 1M sulfuric acid to pH 1 and 2. The absorbance of each Fe solution was measured from 200 nm to 450 nm region.

3.5.2. Calculation of solids and kraft lignin removal

The removal of solid was calculated by following equation:

\[
P_s = \frac{p}{d \times V \times S + Fe} \times 100
\]

(Eq. 3-1)
\[ P_k = \text{removal of solid in liquor (\%)} \]
\[ d = \text{density of black liquor (g/ml)} \]
\[ V = \text{volume of black liquor (ml)} \]
\[ S = \text{solid content of black liquor} \]
\[ Fe = \text{the input of iron chloride hexahydrate (g)} \]
\[ p = \text{weight of precipitate (g)} \]

Lignin content in precipitate was measured through furnace to calculate removal of lignin. Each precipitate (0.1 g) was burned in 575°C for 3 h. In addition, moisture content of precipitate was also measured using oven-drying method.

The lignin content in precipitate was calculated using following equation:

\[
\text{Org}_p = \left( \frac{A_{bef} + Sample \times (1 - MC) - A_{aft}}{Sample \times (1 - MC)} \right) \times 100
\]

(Eq. 3-2)

\( \text{Org}_p = \text{organic compound content in precipitate (\%)} \)

\( \text{Sample} = \text{weight of sample (g)} \)

\( A_{bef} = \text{weight of dried alumina crucible (g)} \)

\( A_{aft} = \text{weight of dried alumina crucible and ash (g)} \)

\( MC = \text{moisture content of sample} \)

The removal of lignin was calculated using following equation:

\[
P_{org} = \frac{p \times \text{Org}_p}{d \times V \times S \times \text{Org}_r} \times 100
\]

(Eq. 3-3)
\[ P_{org} = \text{removal of lignin in liquor (\%)} \]
\[ p = \text{weight of precipitate (g)} \]
\[ \text{Org}_{pp} = \text{organic compound content in precipitate (\%)} \]
\[ \text{Org}_{r} = \text{organic compound content in raw black liquor solid (\%)} \]
\[ V = \text{volume of black liquor (ml)} \]
\[ S = \text{solid content of black liquor} \]

3.5.3. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

ICP-AES (ICP-730ES, VARIAN, Australia) was used to analyze Fe species content in precipitate. Before analysis, pretreatment process was conducted according to EPA 3051 method (Element, 2007). Each precipitate was burned in furnace to eliminate organic compound. Ash (15 mg) was placed in fluorocarbon cell and digested in 10 ml of concentrated nitric acid for 10 min. The cell was heated to 175°C using microwave unit for 10 min. After cooling, the samples were filtered, centrifuged and diluted. The pretreated samples were analyzed using ICP-AES (plasma flow, auxiliary flow = 15.0 L/min, nebulizer flow = 0.73 L/min, gas : Ar).

3.5.4. Gel permeation chromatography (GPC)

GPC was used to analyze precipitation behavior depending on molecular weight of kraft lignin. Raw black liquor and supernatant of each samples which were treated by iron chloride and centrifuged were freeze-dried to obtain solid lignin in solution. Each solid sample (150 mg) was dissolved in 3 ml of pyridine anhydrous and acetic anhydrous (1:1) solution and reacted at 105°C for 2 h with mixing each 30 min. After reaction, the acetylated organic compound was dropped into 20 ml of deionized water to be precipitated. The
The precipitated solid was centrifuged and separated from deionized water. After that, freeze-drying process was conducted. The 5 mg of acetylated samples were dissolved in 1ml of tetrahydrofuran and filtered by using hydrophobic syringe filter (13JP050AN, ADVANTEC, Japan). The molecular weight was analyzed using GPC (1260 Infinity II LC system, Agilent) which was calibrated polystyrene and the flow rate was 0.1 ml/min.
4. Result & discussion

4.1. Chemical composition of black liquor

Analysis of chemical composition of provided black liquor was required to figure out characteristic of black liquor and calculate removal of solid and lignin in black liquor after iron chloride treatment.

Table 1 showed the composition of provided black liquor. Strong black liquor had almost two times more solid content and organic compound than weak black liquor. Density seems to be proportional to organic content. Among the solid, more than half was inorganic substances such as Na, S and Ca. In HPLC analysis for sugar and acetic acid content, arabinose which is component of softwood hemicellulose was detected. Concentration of acetic acid which is from hemicellulose was quite high (5 ~ 7% of solid). It seemed that sugar in black liquor usually come from hemicellulose which was cleaved by kraft pulping process and softwood was used as raw material.
Table 1. Chemical composition of black liquor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Strong black liquor</th>
<th>Weak black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content (%)</td>
<td>33.05 (±0.12)</td>
<td>15.75 (±0.04)</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.14</td>
<td>1.07</td>
</tr>
<tr>
<td>Organic compound in solid (%)</td>
<td>46.64 (±0.25)</td>
<td>48.34 (±0.37)</td>
</tr>
<tr>
<td>Sugar, acetic acid in solid (%)</td>
<td>11.50 (±0.22)</td>
<td>8.43 (±0.15)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>7.94 (±0.40)</td>
<td>5.53 (±0.07)</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.94 (±0.08)</td>
<td>0.58 (±0.04)</td>
</tr>
<tr>
<td>Xylose</td>
<td>2.03 (±0.07)</td>
<td>1.93 (±0.03)</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.59 (±0.10)</td>
<td>0.40 (±0.01)</td>
</tr>
</tbody>
</table>
4.2. Precipitation mechanism of kraft lignin using iron chloride

4.2.1. Sweep flocculation and zeta-potential neutralization

In typical precipitation of colloidal particle using cationic coagulant, both zeta-potential neutralization and sweep flocculation occur as input of cationic coagulant increases. However, in kraft lignin precipitation process using iron chloride, it seemed that only sweep flocculation mechanism worked, but zeta-potential neutralization did not. Especially, critical coagulation concentration which is one of the important characteristics in zeta-potential neutralization didn’t be observed, because iron chloride could not be cationic ion in black liquor.

Figure 4 showed removal of solid in strong black liquor using different input of iron chloride and ethanol-deionized water solvent. When the deionized water (100%) was used as solvent, removal of solid was under 5% regardless of input of iron chloride. Iron chloride generally forms iron hydroxide which is insoluble in water. In other words, removal of solid is likely to increase as input of iron chloride increases. However, removal of solid did not increase. Because kraft lignin has much phenolic hydroxyl and carboxyl group which could bind to metal as ligand, it seemed that kraft lignin in black liquor bound with iron and iron could not form iron hydroxide (Mohan et al., 2006). Coordination site of iron was blocked by kraft lignin and iron could not act as cationic coagulant. For this reason, zeta-potential neutralization mechanism could not work.

In case of ethanol (100%) solvent unlike deionized water (100%) solvent, the removal of solid increased in proportion to input of iron chloride. The biggest difference between ethanol and deionized water solvent was formation of sludge, polymerized metal ion, in black liquor. As the portion of ethanol increased in solvent, the sludge and removal of solid also increased.
(figure 4). In other words, sludge made kraft lignin precipitated and it meant that “sweep flocculation” mechanism worked in ethanol solvent condition. However, in deionized water (100%) solvent, coordination of lignin into iron blocked growth site of iron and prevented metal polymerization. As a result, only monomeric, dimeric of trimeric species could be present in deionized water solvent and sweep flocculation efficiency could be very low (Schneider, 1984). This is because binding with stable ligand made stable substance and hydroxo, oxo bridge couldn’t bind to iron ion (Davis & Edwards, 2017).
Figure 4. Removal of solid in raw black liquor
4.2.2. Effect of solvent in sweep flocculation

Figure 4 showed that ethanol assisted formation of sludge and kraft lignin precipitation. To analyze effect of ethanol in solution, UV-visible spectroscopy was used.

FeCl₃ have different form in solution depending on solution pH. At very low pH, Fe³⁺ is common form. As pH increases, Fe binds with hydroxyl group in water and forms Fe(OH)⁺, Fe(OH)₂⁺, Fe(OH)₃ and Fe(OH)₄⁻ (Oriekhova & Stoll, 2014b). Figure 5 showed the UV-visible spectroscopy absorbance of each FeCl₃ solution from 200 to 450 nm depending on solvent condition. When solvent was deionized water (100%), the peak was formed around 300 nm which was correspond to Fe(OH)₂⁺ and Fe(OH)₃⁺. In addition, when pH was lowered from 3.5 to 2.5, the absorbance around 300 nm decreased and increased at 240 nm. This phenomenon demonstrated that FeCl₃ typically had hydroxide form in water solvent. However, the absorbance at 240 nm was much higher in ethanol solvent than deionized water solvent. Because FeCl₃ had iron ethanolate form when dissolved in ethanol and the structure of iron ethanolate was showed in Figure 6.

In sufficient alkali condition, iron is usually condensed until stable complex is formed by the mechanism shown in figure 3 and the iron condensate is very important in sweep flocculation (Knight & Sylva, 1974). In case of deionized water solvent (100%), ferric ion had Fe(OH)⁺ and Fe(OH)₂⁺ form which was already coordinated by hydroxyl group. In addition, kraft lignin particle in black liquor also competed with hydroxyl group to bind with ferric ion. Because kraft lignin had quite much phenolic hydroxyl group and carboxyl group, kraft lignin could bind with ferric ion as poly-dentate ligand. Poly-dentate ligand usually form very stable compound and iron condensation could be stopped (Davis & Edwards, 2017). For this reason, Fe was weakly hydrolyzed and was
present in monomeric, dimeric or trimeric species (Vilge-Ritter et al., 1999). Iron condensate containing only few iron atoms made small particles and incorporation and entrapment of kraft lignin particles in black liquor could be difficult. Therefore, free Fe$^{3+}$ which do not have any ligand have advantage when olation mechanism worked in black liquor. However, in case of ethanol solvent, most of the Fe had iron ethanolate form and coordination sites of ferric ion were protected by ethanol temporarily. In addition, ethanol also reduced contact between kraft lignin particle and protected ferric ion. Because interface between black liquor and ethanol was observed, when iron chloride dissolved in ethanol mixed with black liquor. It seemed that black liquor had very strong ionic strength and a lot of hydrophilic organic solute which interact with water molecules. This is because high ionic strength and hydrophilic organic solute could interfere interaction between water and ethanol. In other words, iron condensation could be formed more easily in ethanol solvent than in water solvent and sweep flocculation also could work more effectively in ethanol solvent.
Figure 5. UV-vis spectroscopy absorbance of FeCl₃ solution

Figure 6. Structure of iron ethanolate
4.2.3. Effect of lignin properties in sweep flocculation

Black liquor contains several organic compounds which have diverse structures (Mesfun et al., 2014). For example, black liquor contains polysaccharide, extractives, lignin carbohydrate complex (LCC) and kraft lignin which has a wide range of molecular weight. To analyze effect of these organic compounds in sweep flocculation by iron chloride, acid precipitated lignin was used to compare with strong black liquor.

Figure 7 showed that removal of acid precipitated lignin which was dissolved in deionized water and precipitated by iron chloride solution. In this experiment, the concentration of iron chloride was same with the sample shown in figure 4 (input of iron chloride was 3% (w/v)). However, removal of solid showed quite different tendency. When the strong black liquor was used, the maximum removal of solid was about 34%. In case of acid precipitated lignin, the maximum removal of lignin was about 50% which was much higher than 34%. In addition, when solvent of iron chloride was deionized water (100%), precipitation occurred at 5% acid precipitated lignin unlike strong black liquor without formation of sludge. It seemed that the formation of insoluble particle mechanism which is one of the main mechanism of sweep flocculation was activated. When the solvent of iron chloride was deionized water (100%), precipitation of acid precipitated lignin occurred without big sludge. This meant that the possible mechanism was formation of insoluble particle by binding kraft lignin with Fe and sweep flocculation by sludge which contained only few iron atoms.

In case of strong black liquor, it usually contained kraft lignin which had high solubility such as LCC. Therefore, when this highly soluble kraft lignin bound with Fe, the Fe could not form high degree of polymerization (DP) sludge and kraft lignin could not be precipitated because of its high solubility.
(Lappan et al., 1997). As a result, only small amount of kraft lignin was precipitated. However, acid precipitated lignin contained less amount of highly soluble kraft lignin compared with strong black liquor. Table 2 showed sugar and acetic acid content which were derived from hemicellulose and LCC in each kraft lignin. Entire sugar and acetic acid content was reduced by acid precipitating method. Especially, acetic acid content decreased more than half and arabinose was not detected in acid precipitated lignin. In other words, acid precipitate process could screen highly soluble kraft lignin which could hinder formation of both sludge and Fe-lignin insoluble particles. Nevertheless, as acid precipitated lignin concentration increased, the removal of solid at deionized water (100%) decreased. It seemed that the kraft lignin which have high solubility was not removed perfectly.

At ethanol (100%) solvent, it seemed that the formation of sludge was still main mechanism. However, as the formation of insoluble particles was activated by acid precipitation method, removal of solid also increased. In contrary to deionized water solvent, the removal of solid was not reduced as the concentration of acid precipitated lignin increased. This is because the main precipitation mechanism was formation of sludge which was assisted by ethanol.

To analyze these effects of organic compounds more detail, ICP-AES analysis was also conducted. Figure 8 showed Fe content ratio in ash of each precipitated solid. Depending on the solvent of iron chloride solution, Fe content ratio was quite different. At deionized water (100%) solvent, the content ratio of Fe was consistent around 26% regardless of strong black liquor and acid precipitated lignin. This is because formation of sludge was prevented by coordinating of kraft lignin and only formation of insoluble particle and sweep flocculation by low DP sludge were worked. It seemed that phenolic hydroxyl groups and carboxyl groups were bound with Fe stoichiometrically. In case of ethanol solvent, formation of sludge was main mechanism of
precipitation. As a result, sodium ion could be precipitated with kraft lignin when the kraft lignin particle was incorporated inside of sludge and the content ratio of sodium could be very high. However, as the formation of insoluble particles was activated by acid precipitation method, Fe content ratio also could increase and this phenomenon was showed in figure 8.

The molecular weight of kraft lignin in black liquor also seemed to affect sweep flocculation mechanism. Figure 9 showed molecular weight of both raw black liquor and supernatant after precipitation. By iron chloride precipitation, high molecular weight region was considerably reduced. Moreover, relatively low molecular weight region after 8.5 min only showed small variation. This phenomenon meant that the kraft lignin which had high molecular weight could make heavy enough particles more easily by interacting with iron chloride. However, if Fe bound with low molecular weight kraft lignin instead of high molecular weight lignin, particle could not be precipitated.
Figure 7. Removal of kraft lignin in raw black liquor and acid precipitated lignin
Table 2. Contents of sugar and acetic acid in acid precipitated lignin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Strong black liquor solid (%)</th>
<th>Acid precipitated lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>7.94 (±0.40)</td>
<td>3.44 (±0.10)</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.94 (±0.08)</td>
<td>0.70 (±0.02)</td>
</tr>
<tr>
<td>Xylose</td>
<td>2.03 (±0.07)</td>
<td>1.46 (±0.02)</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.59 (±0.10)</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>11.50 (±0.22)</td>
<td>5.59 (±0.05)</td>
</tr>
</tbody>
</table>
Figure 8. Fe species content in ash of precipitate. (iron chloride solvent; (a) = deionized water (100%), (b) = ethanol solvent (100%))
Figure 9. Molecular weight of lignin in raw black liquor and supernatant after precipitation (GPC)
4.2.4. Effect of ions in sweep flocculation

In addition to organic compound, ions in black liquor also can affect sweep flocculation because kraft lignin is usually negative charged colloidal particle in black liquor (Mänttäri et al., 2015). To analyze effect of ion and low molecular weight kraft lignin (Mw < 1000) in black liquor, dialysis of acid precipitated lignin was conducted.

Table 3 showed removal of solid and lignin of dialyzed lignin. By dialysis, the ions in black liquor and low molecular weight kraft lignin which was hard to form heavy flocs was removed. Therefore, increase of removal of solid and lignin was expected because the low molecular weight kraft lignin usually hindering precipitation. However, dialyzed lignin showed poor removal of both solid and organic compound. This is because ions in black liquor such as Na\(^+\) were also removed during dialysis. In table 3, dialyzed lignin which was added some sodium chloride showed increased removal of solid and lignin with dialyzed lignin which was not added sodium chloride. In addition, the increase rate of removal of solid was much bigger in ethanol solvent than deionized water solvent.

According to some studies about precipitation of natural organic matter (NOM) using iron chloride, cations such as Na\(^+\), Ca\(^{2+}\) could partially neutralize negative charge of NOM and make Fe form complexation which was important in precipitation (Davis & Edwards, 2017). Because the kraft lignin also had similar properties with NOM, it seemed that ion effect could be possible reason. In black liquor, high concentration of several cations could partially neutralize negative charge of kraft lignin and could reduce distance between lignin particles according to DLVO theory. As a result, incorporation and entrapment mechanism could be more efficient because lignin concentration per unit volume was relatively high. In ethanol solvent, high DP
of sludge could be formed and this relatively closed distance between kraft lignin particles assisted sweep flocculation. Therefore, removal of solid could increase considerably in ethanol solvent. However, ion effect was relatively weak in deionized water solvent because insoluble particle formation and sweep flocculation by low DP sludge were main mechanism.
Table 3. Removal of solid and lignin (acid precipitated lignin and dialyzed lignin)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lignin concentration</th>
<th>Removal of solid (%)</th>
<th>Removal of lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ethanol solvent</td>
<td>Deionized water solvent</td>
</tr>
<tr>
<td>Acid precipitated lignin</td>
<td></td>
<td>41.79</td>
<td>50.37</td>
</tr>
<tr>
<td>Dialyzed lignin</td>
<td>5 %</td>
<td>22.64</td>
<td>21.02</td>
</tr>
<tr>
<td>Dialyzed lignin (+NaCl)</td>
<td></td>
<td>30.72</td>
<td>22.57</td>
</tr>
</tbody>
</table>
4.3. Precipitation behavior in several conditions

Figure 10 showed precipitation rate of solid and lignin in weak black liquor depending on several precipitation condition such as ratio between iron chloride solution (ethanol) and black liquor and input of iron chloride.

The removal of solid and lignin was proportional to input of iron chloride. Especially, when the input of iron chloride was bigger than 1.5% (w/v), there were steep increase in removal of solid and lignin. The optimum input of iron chloride per 100 ml of black liquor was around 3% (w/v) because the removal of both solid and lignin showed almost no increase at more than 3% (w/v).

In addition to input of iron chloride, the precipitation rate was also affected by ethanol-black liquor ratio. In previous experiments, ethanol usually gave positive effect in sweep flocculation by assisting formation of high DP sludge. However, the removal of solid and lignin was highest at 0.1 ethanol-black liquor ratio and lowest at 1.0 ethanol-black liquor ratio. This is because iron ethanolate and kraft lignin particles had the highest concentration per unit volume at 0.1 ethanol-black liquor ratio. When ferric ion met black liquor which was strong base, ferric ion started metal polymerization very quickly byolation and oxolation mechanism. The high concentration of ferric ion could bind with other ferric ion and metal polymerization occurred very effectively. Besides, the incorporation and entrapment of kraft lignin particles by sludge also could be effective because the concentration of kraft lignin particles per unit volume was high at 0.1 ethanol-black liquor ratio.

However, in 1.0 ethanol-black liquor ratio, the concentration of iron chloride per unit volume was less than one-fifth of 0.1 ethanol-black liquor ratio. In metal polymerization, ferric ion hardly contacted with other free ferric ion and the chance for binding with kraft lignin particles could increase. Moreover,
incorporation and entrapment of kraft lignin particles also could be hard because the concentration of kraft lignin particles per unit volume was relatively low.

Figure 10 (b) showed the organic compound content in precipitated solid. Organic compound content showed opposite result with removal of solid because removal of solid was proportional to sludge formation. However, the variation between maximum and minimum was smaller than 10%.

Figure 10 (c) showed the removal of lignin in black liquor. The removal of lignin was proportional to removal of solid. Therefore, the maximum was observed at 0.1 ethanol-black liquor ratio and it was bigger than 80%. The maximum was observed at 1.0 ethanol-black liquor ratio and it was around 50%.

Figure 11 showed effect of temperature in sweep flocculation. Effect of temperature was compared between room temperature and 65 ℃ which was the typical temperature of black liquor at end of digester. According to some studies, olation and oxolation was affected by temperature (Schneider, 1984). However, the effect of temperature was not observed between room temperature and 65 ℃ and the removal of both solid and lignin.
Figure 10. Removal of solid and lignin content in precipitate. (a) is removal of solid in black liquor, (b) is lignin content in precipitate and (c) is removal of lignin in black liquor.
Figure 11. Removal of solid and lignin in room temperature (25°C) and 65°C. (a) is removal of solid in black liquor and (b) is removal of lignin.
5. Conclusion

In this study, the precipitation of kraft lignin in black liquor was conducted using iron chloride hexahydrate. To analyze mechanism and behavior of kraft lignin, several treatment and analysis were conducted such as acid precipitation and dialysis.

The removal of solid and lignin variation between solvent of iron chloride (ethanol and deionized water) revealed that the main mechanism of precipitation was sweep flocculation by Fe sludge which was from metal polymerization of Fe, not zeta-potential neutralization. When the solvent of iron chloride was deionized water, removal of solid was smaller than 5% regardless of input of iron chloride and there was no formation of big sludge. However, when ethanol was used as solvent, removal of solid increased in proportion to input of iron chloride and formation of sludge was very active. In addition, critical coagulation concentration was not observed. It seemed that kraft lignin could bind to Fe and hinder formation of sludge and precipitation.

Especially, solvent of iron chloride, organic compound and ions in black liquor seemed to affect considerably in sweep flocculation. Ethanol solvent usually gave positive effect in formation of sludge and sweep flocculation. According to UV-visible spectroscopy analysis, high concentration of free Fe$^{3+}$ ion which is favorable species in metal polymerization was observed at ethanol solvent. However, at water solvent, Fe usually had hydroxide form which was already coordinated by hydroxyl group. Formation of interface between ethanol and black liquor revealed that ethanol could prevent binding of kraft lignin and protect coordination site of Fe$^{3+}$ ion. As a result, the formation of sludge could be much more effective in ethanol solvent.
Highly soluble lignin in black liquor also could hinder the sweep flocculation. When highly soluble lignin was removed by acid precipitation, precipitation of kraft lignin occurred in water solvent unlike in strong black liquor without formation of big sludge. This meant formation of insoluble Fe-lignin particles was activated and highly soluble lignin in black liquor which could not be precipitated prevented sweep flocculation. In addition, GPC analysis showed that high molecular weight lignin could be precipitated more easily and low molecular weight lignin hard to be precipitated.

Cation in black liquor seemed to assist incorporation and entrapment of kraft lignin particles. When dialyzed lignin was precipitated, the sample which was added sodium chloride showed much bigger removal of both solid and organic compound in ethanol solvent. It seemed that cations in black liquor partially neutralized negative charge of kraft lignin particle and reduced distance between particles. As a result, kraft lignin could be more dense and incorporation and entrapment by growing sludge worked more effectively.

Removal of solid and lignin in black liquor increased in proportion to input of iron chloride. However, removal of solid and lignin was inverse proportional to ethanol-black liquor ratio. It seemed that the concentration of ferric ion per unit volume was high in low ethanol-black liquor ratio and it make ferric ion could bind each other more easily. Moreover, the concentration of kraft lignin per unit volume was high in low ethanol-black liquor ratio and it make incorporation and entrapment more efficient.

The effect of temperature was analyzed by comparing removal of solid and lignin at room temperature and 65 ℃. However, the effect of temperature was not observed and the removal of solid and lignin was almost same at both temperature.
6. Reference


초 록

염화제이철을 이용한 혼액 내 크라프트 리그닌의 침전거동에 관한 연구

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서울대학교 대학원

크라프트 리그닌은 크라프트 펄핑공정에서 생성되는 부산물로서 주로 농축과 연소를 통해 공정의 에너지원으로 사용되고 있으며 매년 엄청난 양이 생산되고 있다. 이러한 크라프트 리그닌을 고부가가치화하기 위해서는 적절한 침전 및 분리 방법이 요구되지만, 현재 주로 이용되는 산 침전법은 환경 및 부식 등 여러가지 문제를 야기한다. 그러므로 이러한 문제를 해결하기 위하여 산을 이용하지 않고 염기 조건에서 크라프트 리그닌을 침전시켜 분리하려는 노력이 필요하게 되며 다양한 연구들이 진행되고 있다.

본 연구에서는 알칼리 조건에서 크라프트 리그닌을 침전 시키기 위하여 금속염을 이용하여 실험을 진행하였다. 금속염에 의한 크라프트 리그닌의 침전 메커니즘을 분석하기 위하여, raw black liquor와 산 침전 리그닌 그리고 dialysis가 진행된 리그닌을 이용하였다. 응집제로는 염화제이철을 이용하였으며 다양한 용매 조건 (에탄올:물=100:0, 75:25, 50:50, 25:75, 0:100) 및 투입량 조건에
서 용액 상태로 준비되었다. 그 후에 각 200ml의 리그닌 용액은 100ml의 염화제삼철 용액에 투입 되었고 150 rpm에서 30분간 교반되었다. 1시간 후 원심분리기를 통하여 고체와 액체가 분리되었고 분리된 고형분은 동결건조 되었다. 각 용매에 녹인 염화제이철 용액은 용액 내에서의 Fe의 상태를 분석하기 위하여 ultraviolet-visible spectroscopy를 이용하여 분석하였다. 또한 침전 메커니즘을 분석하기 위하여 침전된 고형분은 inductively coupled plasma atomic emission spectroscopy (ICP-AES)와 gel permeation chromatography (GPC) 분석을 진행하였다.

염화제이철에 의한 침전거동을 분석하기 위하여, fresh weak black liquor를 이용하여 실험을 진행하였다. 염화제이철 용액은 다양한 양의 투입량 조건(0.5, 1.0, 1.5, 3.0, 4.0% (w/v)) 및 다양한 부피의 용매에 (10, 33, 50, 100 ml) 녹인 상태로 준비되었다. 그 후에 100ml의 weak black liquor는 염화제이철 용액에 투입되었으며 150 rpm에서 30분간 교반되었다. 1시간 후 원심분리기를 통하여 고체와 액체가 분리되었고 분리된 고형분은 동결건조 되었다. 온도는 상온과 65도에서 각각 진행되었다.

실험결과 크라프트 리그닌은 metal polymerization을 통해 생성된 철 슬러지에 의한 sweep flocculation 기작만 작용하는 것으로 나타났다. 제타전위 중성화의 가장 큰 특징인 critical coagulation concentration은 관찰되지 않았다. 염화제이철의 용매가 증류수일 경우, 침전률은 염화제이철의 투입량에 영향을 받지 않았다. 에탄올이 용매일 경우에는 반대로 침전률이 염화제이철의 투입량에 비례하는 경향을 보였다. 이는 물이 용매일 경우에는 리그닌이 철의 polydentate 리간드로서 작용하여 metal polymerization을
저해하였지만, 에탄올이 용매일 경우에는 에탄올에 의하여 철과 리그닌의 결합이 저해되고 철 슬러지의 형성을 돕는 것으로 사료된다.


다양한 조건에서 침전을 진행한 결과, 흑액은 용매-흑액의 부피비가 0.1인 조건에서 가장 높은 침전률을 보여주었다. 이것은 염화제이철 용액 내 3가 철 이온의 농도가 높아 흑액이 투입되었을 때, metal polymerization이 작용하기에 유리했기 때문이라고 사료
리그닌의 침전률은 염화제이철의 투입량이 증가함에 따라 함께 증가하였지만, 3% (w/v) 보다 많이 투입되었을 경우에는 그 증가량이 매우 작았다. 온도는 염화제이철을 이용한 혼액의 침전에서의 영향을 주지 못하는 것으로 나타났다.

주요어: 크라프트 리그닌, 침전, 염화제이철, 슬러지, sweep flocculation, metal polymerization

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감사의 글

2011년 환경재료과학전공 신입반에 처음 배정받았을 때에는 지금 제 자신이 이렇게 석사학위논문에 감사의 글을 쓰게 될 것이라고는 상상도 못 했을 것 입니다. 하지만, 환경재료과학전공에 진입하고 목재화학연구실에서 석사논문을 마무리하게 되고, 이별을 앞두고 있다고 생각하시나 마음이 복잡해지고 눈물도 날 것 같습니다. 하지만 논문을 마무리하는 것은 단지 인생의 중요한 과정이 끝난 것이고, 연구실을 떠난 다는 것 또한 거처가 바뀌는 것뿐이지 연구실에서 교수님과 선후배님들 그리고 도움을 주신 모든 분과 함께한 시간이 사라지는 것은 아니라고 생각합니다. 그래서 이렇게 감사의 글을 벌여 도움을 주신 모든 분들에게 감사의 뜻을 전하고 싶어 몇 자 남겨봅니다.

먼저 저를 진심으로 걱정해주시고 지도해주시신 최인규 교수님께 감사를 드리고 싶습니다. 교수님께서는 항상 구성원들을 끈끈한 인연으로 묶어 주시고 제가 근심걱정 때문에 기운이 없어 할 때면 진심으로 걱정해주시고 앞으로 나아가라고 말씀해주셨습니다. 아마 절 걱정 해주시던 그 말 한 마디가 없었다면 지금의 제가 과연 있었을까 확신이 들지 않습니다. 하지만, 지금의 저는 연구실 및 석사과정동안 인연을 맺었던 모든 분들이 제겐 소중해졌고 가끔 마음이 악해질 때면 다시금 일어설 수 있는 자신감이 생겼습니다. 취업을 하게 되어 졸업식도 끝나기 전에 조금 먼저 선생님의 걸을 떠나게 되었지만 언제나 제게 해주시던 말씀 잊지 않고 앞으로 나아가겠습니다. 그리고 앞으로 자주 찾아 뵙겠습니다. 선생님 사랑합니다.

학부 및 석사 6년간 목재를 공부를 하면서 전공에 자긍심을 가지도록 가르침을 주신 전공 교수님들과도 감사를 드리고 싶습니다. 항상 학생들을 생각하며 친근한 소재로서의 목재에 대한 가르침을 주신 이전제 교수님, 저의 논문 주제와 깊은 관련이 있는 콜로이드 화학과 실험을 진행함에 있
어 간과하지 말아야 부분을 꼼꼼히 조언해주신 이학래 교수님, 연구자로서의 역량을 키우라고 말씀해주시던 김현중 교수님, 항상 저를 두드려 주시며 격려와 칭찬을 아끼지 않으시던 여환명 교수님, 저의 논문심사 위원장이시면서 그 누구보다 학생들에게 관심을 가지고 사소한 것까지 신경 쏟친 윤혜정 교수님, 항상 웃는 얼굴로 뵐 때마다 힘이 나게 해주신 오정권 교수님이 모두 분들께 너무 감사드리고 제게 주신 가르침 잊지 않겠습니다.

연구실 생활을 하는 동안에 가장 많은 시간을 함께하고 도움을 준 목재화학연구실 선두배님께도 감사의 뜻을 전하고 싶습니다. 목재화학연구실에 잘 녹아들 수 있도록 다소 엄격했지만 막내인 저를 신경 쏟신 선홍누나, 처음에는 무서운 인상이였지만 친근한 분으로 웃으면서 독특하게 저를 지켜주신 수경이형, 연구자로서 실험을 하는 대도를 알려주시고 항상 기본을 잊지 않도록 해준 다정한 세영누나, 연구실장이라는 중책을 맡으셔도 심은 내색하나 보이지 않으며 우리 연구실을 지탱하는 기둥인 준호형, 항상 친근한 태도로 누군가 부지런히 연구하고 사소한 이야기 하나 하나 잘 들어주신 종화형, 항상 배사에 철두철미하지만 때때로 굉장히 상냥하고 보고 있으면 안심이 되는 성민이, 자신보다 연구실을 항상 더 우선시하면서도 목표로 하는 것을 혈쎀 끈기 있게 노력하는 모습이 벗었는 중견형, 재종 막 입학했지만 오랫동안 같이 있었던 것 같은 느낌이 들만큼 착한 다송이, 이 모든 분들에게 저는 꼭 감사의 말씀을 전하고 싶습니다. 비록 연구실을 나와 취직하여 조금 멀어지게 되었지만 맛있는 친절 사서 꺼 찾아 왔겠습니다. 정말로 감사드립니다.

끝으로 지난 길다랗고 긴 학업과정동안 묵묵히 저를 지탱해주신 가족에게도 감사의 뜻을 전하려고 합니다. 항상 부모님 걱정하지말고 하고싶은 것 다 해보라고 해달라는 것은 무슨 일이 있어도 해줄 테니까 포기하지 말고 말씀해주시는 부모님 너무 감사합니다. 저는 부모님께는 철 없는 아들이
겠지만, 앞으로는 자주 찾아 봅고 여태까지 못 다했던 감사를 전하며 잘사는 모습 보여드릴 수 있도록 노력하겠습니다. 어렸을 때부터 항상 인생 선배로서 목욕히 앞서 가야할 길을 깨닫게 해준 큰누나, 나이 차이도 많이 나는 데 항상 솔한 건 사주면서 친형처럼 너무 따뜻하게 대하여 주신 큰매형, 항상 다정하게 감싸주고 사소한 것에도 공감해주고 최근에는 조카까지 생겨 너무 행복해보이는 작은누나, 아직은 조금 어색하지만 처남이라 불리 주실 때면 행복한 느낌이 들게 해주시는 작은 매형 감사합니다.

만약 저의 인생에서 제일 잘한 선택을 꼽으라고 한다면 목재화학연구실에서 공부한 이 시간을 떠올리게 될 것 같습니다. 석사라는 작은 성과를 내면서 교수님과 선후배님을 포함한 많은 사람들과 쌓은 인연은 학위 이상의 가치를 가진다고 믿어 의심치 않습니다. 앞으로 많은 바 역할을 다하며 모두가 본인이 가지고 있는 소망을 이루며 행복하게 살았으면 좋겠습니다. 그리고 응원하겠습니다. 감사합니다.

2019년 2월
연승현 올림