การแยกลิกนินจากน้ำยางดำโดยกระบวนการไฟฟ้าเคมี

นางสาวศศิวิมล โชตินันทเศรษฐ์

SEPARATION OF LIGNIN FROM BLACK LIQUOR BY ELECTROCHEMICAL PROCESS

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Environmental Management

(Interdisciplinary Program)

Graduate School

Chulalongkorn University

Academic Year 2007

Thesis Title   SEPARATION OF LIGNIN FROM BLACK LIQUOR BY
ELECTROCHEMICAL PROCESS

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ศศิวิมล โชตินันทเศรษฐ์ : การแยกลิกนินจากน้ำยางดำโดยกระบวนการไฟฟ้าเคมี. (SEPARATION OF LIGNIN FROM BLACK LIQUOR BY ELECTROCHEMICAL PROCESS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร. พิชญ รัชฎาวงศ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ดร. วิบูลย์ ศรีเจริญชัยกุล, 101 หน้า.

วัตถุประสงค์ของงานวิจัยนี้มีเพื่อศึกษาและอธิบายความสัมพันธ์ของตัวแปรที่ทำการศึกษาต่อประสิทธิภาพการแยกลิกนินจากน้ำยางดำโดยกระบวนการไฟฟ้าเคมีด้วยการออกแบบการออกแบบเชิงแฟกทอเรียลแบบ 2^3 ตัวแปรที่ทำการศึกษา คือ ความหนาแน่นของกระแสไฟ ระยะเวลาการเกิดปฏิกิริยา และปริมาณของแข็งเริ่มต้น

จากผลการศึกษาพบว่าค่าพีเอชที่เหมาะสมสำหรับการแยกลิกนินด้วยกระบวนการเคมีไฟฟ้าคือ พีเอช 6 พบได้ว่า ประสิทธิภาพการแยกสูงสุด สูงถึง 82.86% ซึ่งเป็นผลจากขั้วอลูมิเนียม 14.89% ปฏิกิริยานี้เกิดขึ้นที่ระดับสูงของความหนาแน่นไฟฟ้า ระดับต่ำของระยะเวลา และระดับสูงของจำนวนของแข็งเริ่มต้น สำหรับขั้วเหล็กประสิทธิภาพสูงสุดของการแยกลิกนินซึ่งเกิดขึ้นที่ระดับสูงของทั้งสามปัจจัยคือ 78% และเป็นผลจากการใช้ขั้วไฟฟ้า 10.03% ที่สภาวะเหล่านี้ ถือได้ว่าเป็นสภาวะที่เหมาะสมที่สุดต่อการแยกลิกนินจากน้ำยางน้ำ ด้วยกระการไฟฟ้าเคมี ที่ได้จากการศึกษาโดยการออกแบบเชิงแฟกทอเรียลแบบ 2^3 ตัวแปร ในขณะที่พีเอช 8 และ 7 นั้น ลิกนินไม่สามารถตกตะกอนได้ สมการความสัมพันธ์ของตัวแปรที่ทำการศึกษา กับประสิทธิภาพในการตกตะกอนของลิกนินที่พีเอช 6 ได้ถูกสร้างขึ้นสำหรับทั้งขั้วอลูมิเนียม และขั้วเหล็ก ในบรรดาตัวแปรที่ทำการศึกษาจะพบได้ว่า ปริมาณของแข็งเริ่มต้นมีความสำคัญกับการตกตะกอนของลิกนินมากที่สุด รองลงมาคือความหนาแน่นของกระแสไฟ และระยะเวลา อย่างไรก็ดี ความสามารถในการพยากรณ์ของสมการนั้นถูกจำกัดเนื่องจากยังมีตัวแปรบางตัวที่มีผลต่อการตกตะกอนของลิกนินซึ่งยังไม่ได้นำมาศึกษาและรวมอยู่ในสมการ ข้อดีของการตกตะกอนด้วยไฟฟ้าเคมีเมื่อเทียบกับการลดพีเอชอย่างเดียวนั้น คือ ประสิทธิภาพของการตกตะกอนที่ได้โดยการใช้สารเคมีอันตรายในปริมาณที่น้อยกว่า ค่าพีเอชของน้ำเสียที่เหลือที่อยู่ในเกณฑ์มาตรฐานน้ำทิ้ง และไม่มีก๊าซอันตรายเกิดขึ้นเช่นการลดพีเอช การประเมินทางเศรษฐศาสตร์พบว่าขั้วอลูมิเนียมมีต้นทุนที่ถูกกว่าประมาณหนึ่งจุดสองเท่าเมื่อเทียบกับขั้วเหล็ก

สาขาวิชา การจัดการสิ่งแวดล้อม   ลายมือชื่อนิสิต Sasi vimon C.
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#4989506020   : MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORD: LIGNIN SEPARATION / ELECTROCOAGULATION / ELECTROCHEMICAL PROCESS

SASIVIMON CHOTINANTASAETH : SEPARATION OF LIGNIN FROM BLACK LIQUOR BY ELECTROCHEMICAL PROCESS. THESIS PRINCIPLE ADVISOR : ASST. PROF. PICHAYA RACHDAWONG, PH.D., THESIS COADVISOR : VIBOON SRICHAROENCHAIKUL, PH.D., 101 pp.

The objectives of this study were to understand and quantify the relationship of factors affecting lignin recovery and to study the optimal condition for separation of lignin from black liquor by electrochemical process using 2^3 factorial design where current density, time, and initial solids were varied. From the result, it was found that optimum pH for lignin recovery is at pH 6 where highest recovery of lignin using aluminum electrodes was 82.86% where 14.89% was the result of electrochemical process. The highest recovery of lignin using iron electrodes was 78% where 10.03% was as the result of electrochemical process. The conditions of highest recovery were considered to be the optimum lignin recovery conditions for aluminum and iron electrodes yielded from this 2^3 factorial design experiments while to recovery at pH 8 and 7 were not accomplished. The models of lignin recovery at pH 6 were constructed was found that among all factors, initial solids content had the highest positive effect on lignin recovery then current density and time. But, the ability of models are limited due to other factors that have major impact on lignin recovery, which had not included in the model. However, lignin recovery with electrochemical process alone has several advantages over acidification alone. These advantages included less amount of caustic chemical used to gain the same recovery, control of pH of remaining black liquor, and no production of corrosive gas such as sulfur like in acidification process. In economics aspect, recovery by aluminum electrode is about 1.2 times more efficient than iron electrodes.

Graduate School

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(Interdisciplinary Program)   Principle Advisor's Signature...............

Academic Year: 2007   Co-advisor's Signature................

ACKNOWLEDGEMENTS

This work would not have been possible without support from many persons. First of all, I would like to thank the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn Univerysity for providing me full scholarship and the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM) Laboratory, Chulalongkorn Univerysity for laboratory facility and equipments.

SCG Paper PLC for supporting of black liquor sample and Mr. Werawit Klangboonserm for being a great coordinator and kindly provided information supporting the experiment.

I also would like to thank all the thesis committee for generously spare their time to read my thesis and attend my presentation especially Dr. Adisak Vorakunpinij who is the external committee member from SCG Paper PLG, my thesis Co-advisor, Dr. Viboon Sricharoenchaikul for giving me opportunities, help, and valuable advices, and my thesis principle advisor, Dr. Pichaya Rachdawong, who always being patient with me and give me opportunities, great advices, supports, and encouragement. Without you, life would be a lot harder.

The most important people in my life, my family; mom, dad, Bebe, and Joseph, for your understanding, patient, love, care, support, encouragements, advices, prayers, and many more that could not be all written here. I thank God for having you guys in my life. I love you guys so much. Without you I would not be able to get through all these hard times for sure. And to all of my friends, brothers, and sisters in Christ especially Miss Runchana Tiemsurawatch, Miss Siripat Suwatpanich, Mr. Wipart Wiboonpanuvej, and Mr. Susunt Pattarthammas for their support, love, and prayer and for always being there for me no matter what. I really do appreciate those times, seriously do.

Last, to the person behind all my success, I would like to thank you, Lord, for all you have been providing for me: great family, best friends, understanding advisor, wisdom, strength, love, and all good and bad times in my life. I am so glad I know you and have you in my life. I thank you for every minute of my life.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Introduction and Problem Statement

The growth of economics of both Thailand and other countries nowadays has increases the amount of paper being used. The pulp and paper industry is accounted as an integral part of many countries' economy. In the U.S. alone, the industry employs 1.5 million people and is one of the top ten manufacturing employers with an estimated payroll of $51 billion (Chimack, Walker, and Miller, 2003). Pulping industry is one of the industry that consume a lot of water in their production process where one ton of pulp needs about 40-60 m^3 of water (Pichainarong, 2002). It results in vast amount of wastewater being produced each day. In Thailand, pulp is produced about 1 million tons/year (The federal of Thai industries, [online]). Though not as large when compares with world's major players, but still considered as a very important industrial sector of Thailand from the country's economy size. And the amount of wastewater, black liquor, produced of each pulping industry can be ranged from hundred to thousand tons per day.

Black liquor from pulping process is a complex mixture of inorganic and organic components such as lignin residue, water, and the chemicals used for the extraction. However, the main component of black liquor is lignin, which considered biomass. Pulp mills will burn black liquor in order to recover pulping chemicals, white liquor, and energy back to the pulping and papermaking operation. Due to its large volume, black liquor represents the fifth largest source of energy in the U.S(Baxter, [online]). However, lignin, which in one of the most abundant natural raw material available can be recovered and used in many applications. Nowadays, applications of lignin have expanded into literally hundreds of applications. The applications of lignin are such as construction binder, food additives, fat purification, and additive in lignin biopolymer. It also can be used as raw material in the production of vanillin, which is widely used as an ingredient in food flavors, in pharmaceuticals and as a fragrance in perfumes and

odor-masking products(Lignin Institute, [Online]).

Lignin from kraft process, which is the main pulping process that account for about 95% (Gosselink et al, 2004) of the world production, is normally separated from black liquor using acidification or membrane filtration. However, there are problem associated with these technologies. For membrane separation, problems are the high cost of membrane itself and the maintenance cost due to membrane fouling and corrosiveness of black liquor. For acidification, vast amount of acid is needed to lower pH of alkali black liquor from 12 -13 to acid range, where the optimum range of lignin precipitation was found to be at pH 3 (Pichainarong, 2002). Another problem is the need to neutralize the remaining black liquor solution after lignin precipitation before discharging.

In this research, electrochemical process is introduced for lignin precipitation where a pair of iron and a pair of aluminum electrodes were used. The metal ion formed in the process was expected to aid the precipitation of lignin from alkali black liquor.

1.2 Objectives

- To understand and quantify the relationship of factors affecting lignin recovery
- To study the optimal condition for separation of lignin from black liquor by electrochemical process using 2^3 factorial design experiment

1.3 Scope of Work

1. Black liquor being used in this study was from SCG Paper PLC, Banpong Pulp Mill, Ratchaburi, Thailand, which use Eucalyptus as raw material and undergo soda pulping process.
2. Lignin recovery was done using batch reactor.
3. Two types of electrodes, a pair of aluminum and a pair of iron electrodes, were used in the experiment.
4. The initial pH of black liquor prior to the electrochemical process was adjusted to 3 levels, which are 8, 7, and 6.

5. The 2^3 factorial design or design of experiment was used with factors of current density, reaction time, and initial solids content being varied.

1.4 Experimental Process

```
                          ┌─────────────────┐
                          │  Black Liquor   │
                          └─────────────────┘

┌─────────────────────┐  ┌─────────────────────┐  ┌─────────────────────┐
│  pH adjustment to 8 │  │  pH adjustment to 7 │  │  pH adjustment to 6 │
└─────────────────────┘  └─────────────────────┘  └─────────────────────┘
```

Experiment

-   Current density (X_A); mA/cm^2
-   Reaction time (X_B); minute
-   Initial solids content (X_C); %

Results analysis

Construction of model
using 2^3 factorial design

Results analysis and conclusion
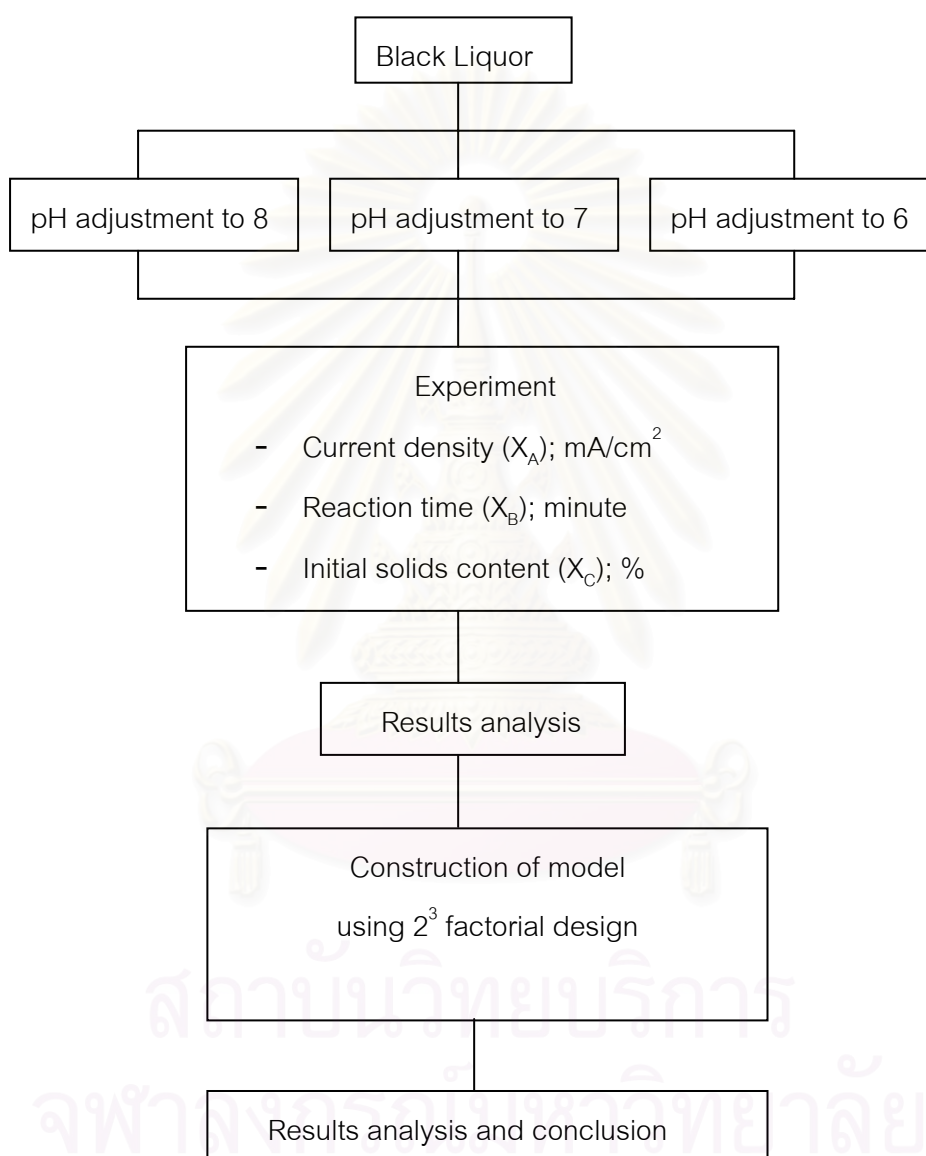
Figure 1.1 Experimental process

1.5 Expected Results

1. The quantitative relationship of factors affecting lignin recovery will be described through model.

2. The optimal condition for lignin recovery can be recognized from the experiment.

3. The contribution and/or limitation of selected factors of the model can be noticed from the model and model accuracy.

CHAPTER II

THEORETICAL BACKGROUNDS AND LITERATURES REVIEW

2.1 Theoretical Backgrounds

2.1.1 Lignin (Georgia Institute of Technology, [online], Glazer, 1995)

Wood is composed of many chemical components, primarily extractives, carbohydrates, cellulose, hemicellulose, and lignin. Lignin is the brownish colored chemical, which is one of the primary components in plant cell walls, other than cellulose and hemicellulose. It acts as glue that holds cellulose, which is the fibrous component and hemicellulose, which generally is heteropolysaccharides of wood together. It also help decreases the permeation of water through the cell walls and help defense against degradation by impeding penetration of destructive enzymes through the cell wall. Lignin is the most abundant aromatic polymer on earth. Plant biomass consisted about 45% of cellulose, 30% of hemicellulose, and 25% of lignin. Lignin contains very complex natural polymers with many random couplings consisting of phenylpropane (C_9) units. Figure 2.1 shows the generalized structure of lignin by the American Chemical Society. The direct precursors of lignin are three alcohols, the lignols; coniferyl alcohol, *p*-coumaryl alcohol, and sinapyl alcohol, which are bonded by C-C and ether (C-O-C) linkage. Figure 2.2 shows the structure of the three lignols and Figure 2.3 shows common linkage of lignin. Lignin can be divided into hardwood (angiosperm) lignin, softwood (gymnosperm) lignin, and grass or annual plant (graminaceous) lignin. Guaiacyl lignin is composed principally of coniferyl alcohol units and generally is found is softwood. Guaiacylsyringy lignin contains monomeric units from coniferyl and sinapyl alcohol, which normally found in hardwood. Graminaceous lignin is composed mainly of p-coumaryl alcohol units. However, the exact chemical structure of lignin is not known.
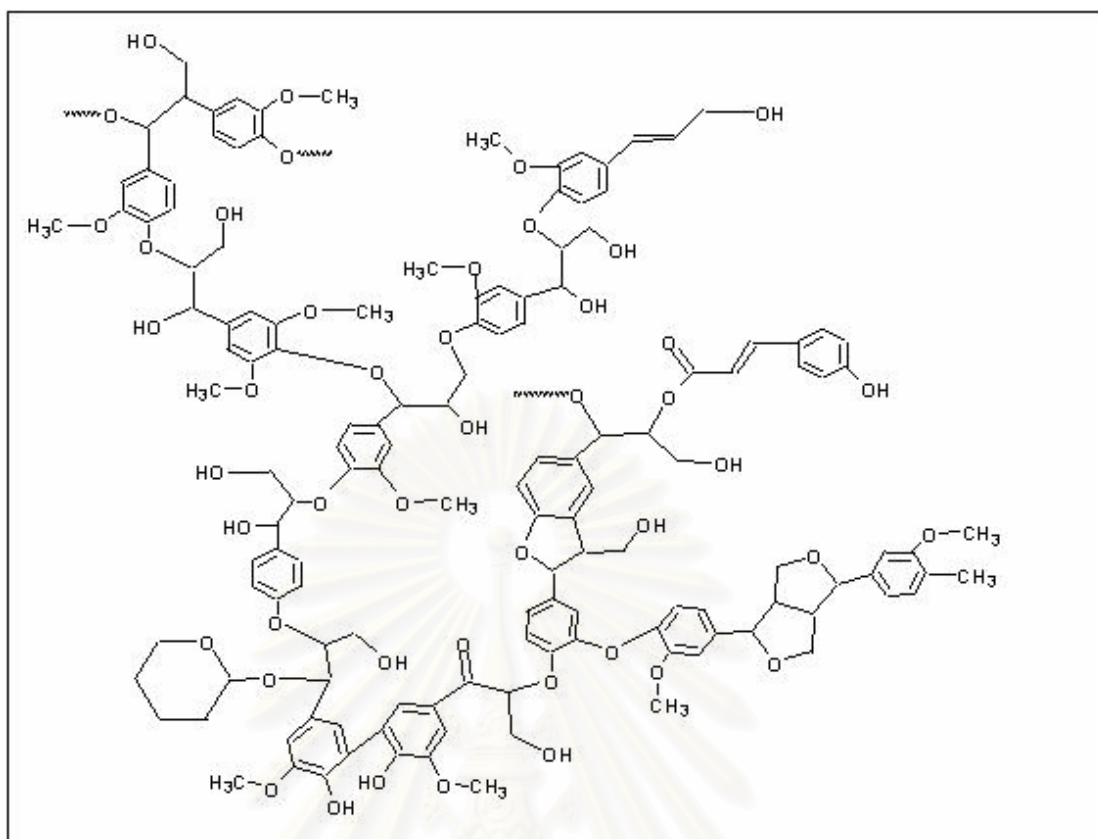
Figure 2.1 Generalized structure of lignin
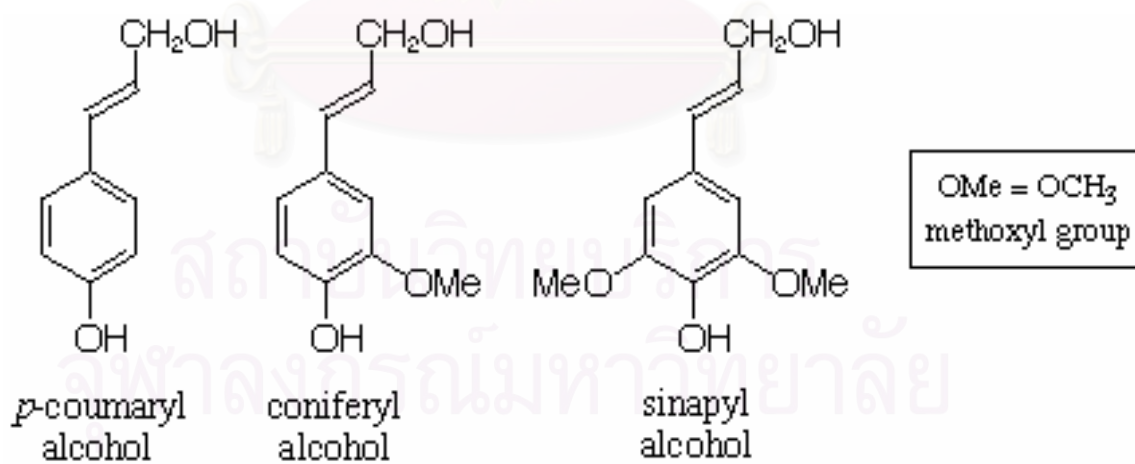
Figure 2.2 The three lignols (Brooks, [online])
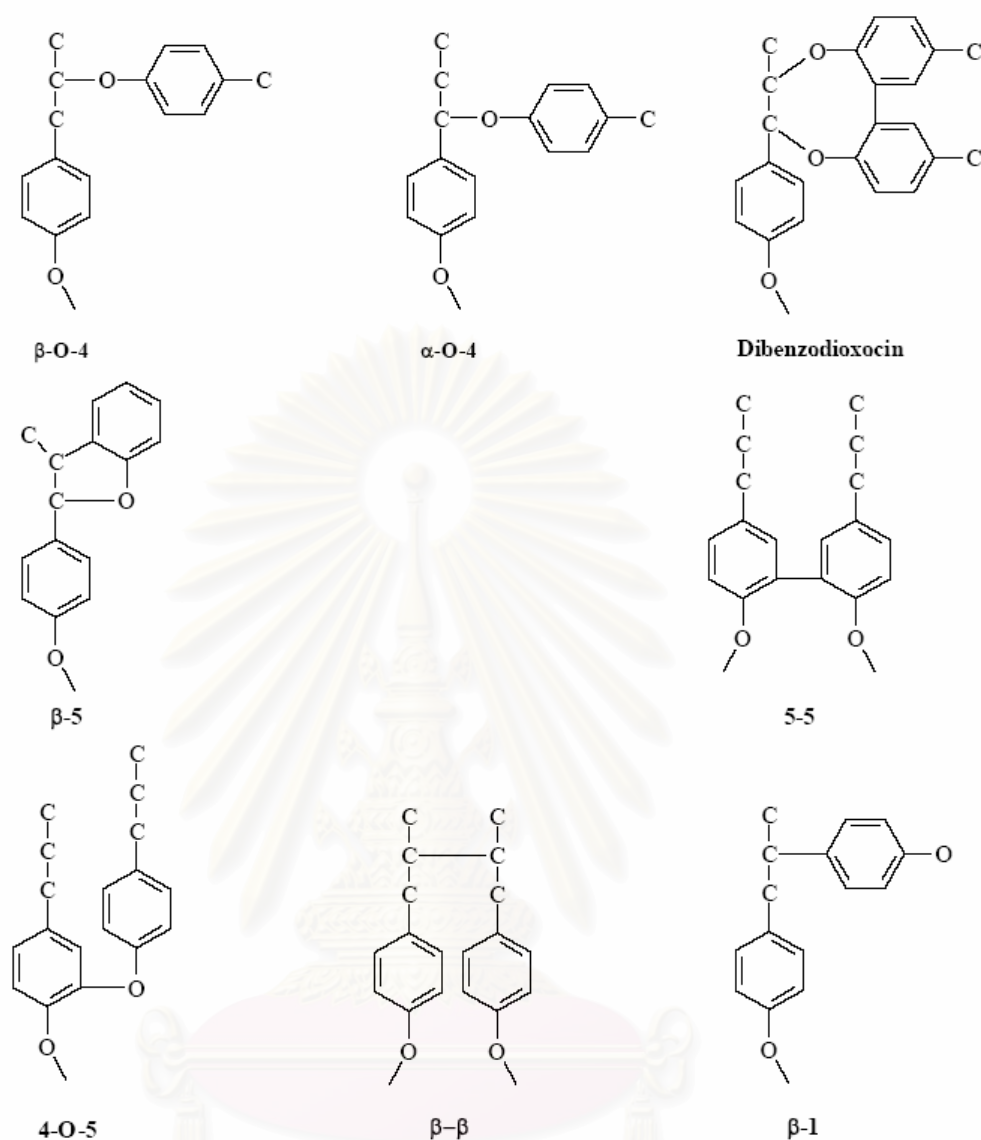
Figure 2.3 Common linkage of lignin (Georgia Institute of Technology, [online]).

2.1.2 Pulping Process (Lignin institute, [Online], Mohanty, 1997)

Pulping is the process that reduces wood to a fibrous mat by separate cellulose from lignin and other chemicals. Woods, raw materials, that are used for pulping process include pine, bamboo, rubber wood, bagasse, eucalyptus, and etc. Only 40% of raw material input is represented the solid yield, the other 60% is the liquid by-product and has to be treated further. Pulping process, generally, can be classified as chemical, mechanical, or semi-chemical. The qualities yield will varied depend on the process and will varied in applications as well.

2.1.2.1 Chemical Pulping Process

Chemical pulping uses chemicals to separate cellulose from lignin. This creates pulps with different properties that can be used for higher quality paper. In chemical pulping, wood chip is cooked in a digester at elevated pressure and temperature. An alkaline (kraft) or acidic (sulfite) chemicals is used to break the chemical bonds of lignin and allows lignin to dissolve, then separation between fiber and lignin can occur. Chemical pulping can be divided into 2 main processes.

a) Sulfite Process

Sulfite Process is an acid chemical pulping process. It produces wood pulp which is almost pure cellulose fibers by using various salts of sulfurous acid to extract the lignin from wood chips in digesters. The salts used in the pulping process are either sulfites (SO_3^{2-}), or bisulfites (HSO_3^-), depending on the pH. Sulfite pulping was the dominant process for making wood pulp until it was surpassed by the kraft process in the 1940s. Sulfite pulps now account for less than 10% of the total chemical pulp production. The quality of pulp from sulfite process is lower compares to pulp from kraft pulping process. This is because the hydrolysis of some cellulose by acidic conditions. Therefore, the pulp yield is not as strong as kraft pulp fiber. The important by-product of sulfite pulping is lignosulfonates, which are used in making concrete, drilling mud, drywall, and etc.

b) Alkaline Process

i. Soda Process: It is an alkaline process where sodium hydroxide is used as cooking liquor in the digester. Pulp is cooked in the digester for about 10 hours under high pressure and temperature. The digestion process will decomposes the binding, non-cellulose material such as lignin and resins, from the fibers.

ii. Kraft Process: It is similar to Soda Process but with the addition of Sodium Sulfite in the cooking liquor. Sodium sulfate will act as buffer, which

allows digestion to be possible at lower pH, thus, reducing damage to the fibers and producing pulp with higher strength.

2.1.2.2 Mechanical Pulping Process

Mechanical Pulping is the process where wood is grounded into fibers by disk refiners or grindstones. Lignin is rarely separated from cellulose in this process. Mechanical pulping process provided low grade pulps with high color(as a result for remaining lignin) and relatively short fibers (due to cut of fiber) but provides a high yield. About 95% of wood input are converted into pulp.

2.1.2.3 Semi-Chemical Pulping Process

Semi-chemical pulping uses a combination of chemical and mechanical processes. The wood chips are partially cooked for 10-20 min. at a temperature of 175-185 °C with aqueous solution of sodium sulfite and sodium carbonate. The remainder of the pulping is further defiberized mechanically in disc refiners and washed.

2.1.3 Black Liquor

Black Liquor is a very dark wastewater resulting from pulping process of pulp and paper industries. It composed of soluble and colloidal organic and inorganic components coming from the digestion of wood and extracted in the aqueous media from the cellulose fibers during the washing process. The chemicals that are the component of black liquor are such as degraded lignin, extractable soap or tall oil, hemicellulose and hydroxyl acid, and many species of inorganic such as NaOH, Na_2CO_3, Na_2SO_4, NaS, and small amounts of Ca, Mg, Si, etc. depend on type, age, and season of wood feedstock, and the digestion and washing process. Therefore, the composition of black liquor can vary considerably. (Chao, [online]) However, it usually has dark brown color, high in pH (result from alkaline process, which is the main pulping process), BOD, and TDS.

2.1.4 Pulping Process of SCG Paper PLC

SCG Paper PLC pulp mill is located in Banpong, Ratchaburi. At Banpong pulp mill, there are two main pulping process, which are chemical pulping process and semi-chemical pulping process using eucalyptus as raw material. However, in this study, black liquor being used was from chemical pulping process where soda pulping process was used. The process involved washing of raw materials (eucalyptus wood), chemical digestion under high temperature, pulp washing, pulp cleaning, bleaching, and paper making. The flow chart of this chemical pulping process is shown in Figure 2.4 where it is provided by SCG Paper PLC and chemicals associated with the black liquor from Banpong pulp mill is shown in Table 2.1.
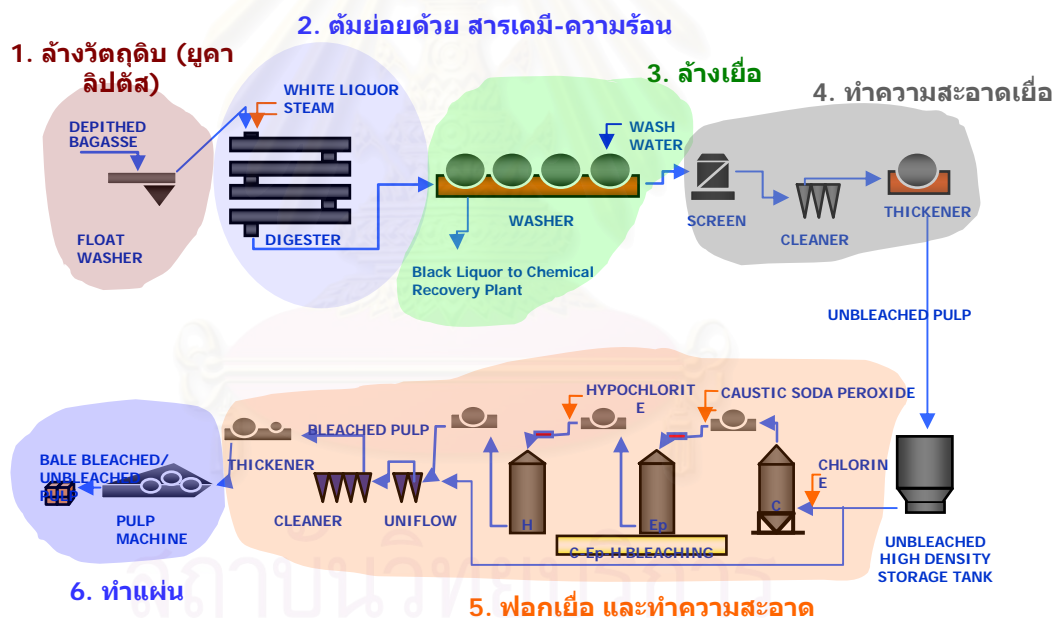
Figure 2.4 Chemical pulping process of SCG Paper PLC

Table 2.1 Chemicals characteristic of black liquor from Banpong pulp mill

Parameters	Unit	July 9, 2007	October 29, 2007	December 11, 2007
C	wt.%	17.84	19.6	26.5
H	wt.%	3.45	4.8	4.9
N	wt.%	2.97	2.5	3.1
S	wt.%	0.29	0.17	0.41
Cl	wt.%	1	1	1.1
Na	wt.%	19.3	19.4	19.3
K	wt.%	2	1.7	2.2
SiO_2	wt.%	0.16	0.14	0.09
Heating value	kcal/kg	2675	2565	2797

2.1.5 Lignin Recovery (Lignin Institute, [online], Meister, 2000)

Lignin, which has been increased in its important in many industrial can be derived from plants. In order to use, lignin has to be extracted from woods. Each extraction process, however, produces material of different composition and properties. Physical and chemical properties of lignin are different depending on the extraction technology from plant, which alter the chemical and functional group composition of lignin and make lignin extremely heterogeneous. Because of these differences, unique names are applied to each lignin preparation and should be used when describing these materials.

Methods for lignin recovery from plants are, for examples, alkali process, sulfite process, organic solvent extraction, and ball milling. However, among them, only alkali and sulfite process are currently become main sources of commercial lignin.

2.1.5.1 Alkali Lignin

Alkali lignin is produced from kraft and soda pulping processes. They have low sulfur content (lower than 1.6 wt. %) present as thioether linkages. They are water-insoluble, nonionic polymers that have molecular weight of 2,000 to 15,000.

2.1.5.2 Lignosulfonate

Lignosulfonate is lignin, which resulted from sulfite process. They contain approximately 6.5 weight percent sulfur present as ionic sulfonate groups on the alkyl chains of the lignin. They are very water-soluble and commonly have molecular weights between 10,000 and 40,000. However, the molecular weight can be as high as 150,000.

2.1.5.3 Organosolv lignin

Organosolv Lignin is produced from a number of different organic solvent-based systems. The water insoluble products produced in these systems are usually purified and contain a very high percentage of lignin. These lignin products are currently not marketed because of unfavorable economics associated with the production of pulp using these systems.

2.1.5.4 Milled Wood lignin

Milled Wood lignin is produced from solvent extraction and purification of finely ground wood, which resulting in powder. Yield is about 25% of the total lignin. Milling will also disrupts the morphology of lignin in wood and may cause the formation of some functional groups on the produced lignin.

2.1.6 Lignin Extraction from Black Liquor

Normally, after the pulping process, black liquor, which has high lignin content, will pass through the recovery boiler where black liquor is burned to generate heat and conduct electricity and chemical used in the digesting process can be recovered. However, the applications of lignin encourage people to separate lignin out for other valuable applications.

Lignin in kraft black liquor commonly is presence in form of negatively charge colloid dissolved in alkali solution. It can be separated using acid precipitation, which will destroy the colloid stability of black liquor (Norgren et al., 2001), membrane filtration, and a new proposed technique, electrochemical process.

2.1.7 Electrochemistry (Sawyer et al., 1994, Sinsomboon, 2006)

Electrochemistry is a concerned with the relationships between electrical and chemical phenomena. The reactions will take place at the interface of an electronic conductor (the electrode) and an ionic conductor (the electrolyte). The chemical changes are resulted by the electricity applied or vice versa. However, in this case, electricity will be applied to induce the chemical reactions, oxidation-reduction reactions, at the electrodes.

2.1.7.1 Electrochemical Cell

Electrochemical cell consisted of DC voltage source, electrolyte, and electrodes connected as shown in Figure 2.5. An electrolyte is a substance containing free ions that behaves as an electrically conductive medium. Electrolytes commonly exist as solutions of acids, bases or salts. An electrode, which connected to the voltage source in an electrochemical cell, is referred to as either an anode or a cathode. The anode is defined as the electrode at which electrons leave the cell and oxidation occurs, and the cathode as the electrode at which electrons enter the cell and reduction occurs. Each electrode may become either the anode or the cathode depending on the voltage applied to the cell. When the electric current is applied, cation will move toward the cathode and anion will move toward the anode. Thus, the oxidation and reduction occur at the electrodes. The reactions occur at the electrodes are as followed.

At anode:

$$M_{(s)} \longrightarrow M_{(aq)}^{n+} + ne^- \qquad (1)$$

At cathode:

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^- \qquad (2)$$
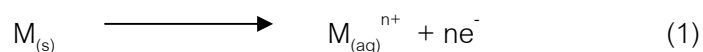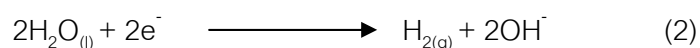
Outside solution, the conductivity will occur thru the movement of electrons in the wire, while in the solution, electric current is conducted thru movement of ions.
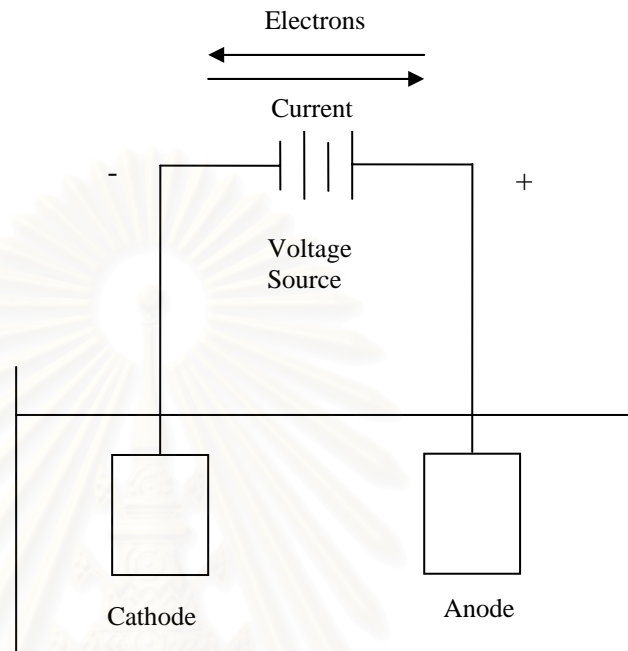
Figure 2.5 Electrochemical cell

2.1.8 Coagulation Mechanisms (Peavy et al., 1988)

The coagulation in water treatment plant, usually by the addition of trivalent metallic salts, is believed to occur by four mechanisms. These include ionic layer compression, adsorption and charge neutralization, entrapment in a flocculent mass, and adsorption and interparticle bridging.

2.1.8.1 Ionic Layer Compression

The quantity of ions in the water surrounding a colloid has an effect on the decay function of the electrostatic potential. The higher ionic concentration will compress the layer between particles. And if this layer is sufficiently compressed, the attraction force or van der Waals force between particles will take effect.

2.1.8.2 Adsorption and Charge Neutralization

The ionization of the coagulant, for example, aluminum sulfate, will produces sulfate anions(SO_4^{2-}) and aluminum cations (Al^{3+}). Sulfate ions may remain in this form or combine with other cations. However, Al^{3+} cations will react immediately with water to form variety of aquometallic ions such as $AlOH^{2+}$, $Al(OH_2)$, $Al_7(OH_{17})^{4+}$, and $Al(OH)_3$, and hydrogen. These aquometallic ions will become part of the ionic cloud surround the colloid and adsorbed onto the surface of the colloid. The surface charge will then be neutralized and resulting in lower electrostatic potential and attraction of colloid

2.1.8.3 Sweep Coagulation

From above, the last product of hydrolysis of alum is aluminum hydroxide, $Al(OH)_3$. It forms in amorphous, gelatinous flocs that are heavier than water and settle by gravity. Colloids may become entrapped in a floc as it is formed, or they may become enmeshed by its "sticky" surfaces as the flocs settle.

2.1.8.4 Interparticle Bridging

In coagulation process, synthetic polymers maybe used instead of or in addition to the metallic salts. These polymers may be linear or branched and are highly surface reactive. Therefore, several colloids may become attached to one polymer and several of the polymer-colloids groups may become enmeshed and result in a settleable mass.

2.1.9 Lignin Concentration Determination

Lignin concentration can be measured using UV spectrophotometry, usually at wavelength of 280 nm., which is a nondegradative method of lignin analysis. This method is a method for phenolic group determination, which has earned widespread acceptance as a rapid and simple method and adaptable to samples of small size. However, the calibration curve of known lignin concentration will have to be constructed prior to the sample determination (Saake and Lehnen, 2007, Steinbuchel, 2001).

2.1.10 Use of Lignin

The applications of lignin are various. Lignin can be used in many fields due to its dispersing, binding, complexing, and emulsion-stabilizing properties. However, among all the applications, lignin is used as an additive in concrete mixtures the most. Lignin is added to concrete to reduce the amount of water necessary in a concrete to reach a certain fluidity. Additionally, lowering water content improves the concrete's final strength. Second, is the use of lignin as an additive to animal feed where lignin is used to improving pellet quality and production efficiency due to its excellent bonding quality. The animal feed-pellets become harder and dust development is reduced. Third is as an additive to duroplasts where lignin is added to aminoplast or phenoplast glues in the production of particle board. Lignin will improves the adhesive properties at low temperatures. Other applications of lignin are, for examples, additives for the composite colors, additive in crude oil well drilling muds, chemical raw material for the synthesis of vanillin, undergo pyrolysis to form noninonic surfactants for oil recovery (lignin Institute, [online], Saake and Lehnen, 2007, Steinbuchel, 2001).

2.1.11 Factorial Design (Montgomery, 2001)

Factorial design or design of experiment (DOE) is the design of experiments where in each complete trial or replication of the experiment, all possible combinations of the levels of the factors are investigated. The effect of factors can be divided into 2 types; main effect and interaction effect. Main effect refers to the change in responses produced by a change in the level of a primary factor of interest in the experiment. Interaction effect is the change in responses produced by a combination of factors. With factorial design, main effect of each factor being study and interaction effect between factors acting together can be calculated quantitatively. The factorial design can help prevent misleading conclusions when the interactions between factors may present and it also allow the effects of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experiment conditions.

2.1.11.1 The 2^k Factorial Design

The 2^k factorial design is a type of factorial experiment where there are k factors to be studied and each at only 2 levels. In this design, since there are only two level for each factor, it is assumed that the response is approximately linear over the range of the factor levels chosen.

2.1.11.2 The 2^3 Factorial Design

In this design, there are three factors; A, B, and C and each at two levels to be studied. The eight treatment combinations can be written as design matrix where -1 and +1 are the notations represent the two levels of each factor. The design matrix is as followed and the geometric representation of 2^3 factorial design is shown in Figure 2.6.

Run	Labels	A	B	C	Resultant (Y)
1	(1)	-1	-1	-1	Y_1
2	a	+1	-1	-1	Y_2
3	b	-1	+1	-1	Y_3
4	ab	+1	+1	-1	Y_4
5	c	-1	-1	+1	Y_5
6	ac	+1	-1	+1	Y_6
7	bc	-1	+1	+1	Y_7
8	abc	+1	+1	+1	Y_8

Following Montgomery, 2001, Main effects and interaction effects can be calculated as follow:

Main effect A: $\quad E_A \quad = (y_2+y_4+y_6+y_8)/4 - (y_1+y_3+y_5+y_7)/4$

Main effect B: $\quad E_B \quad = (y_3+y_4+y_7+y_8)/4 - (y_1+y_2+y_5+y_6)/4$

Main effect C: $\quad E_C \quad = (y_5+y_6+y_7+y_8)/4 - (y_1+y_3+y_5+y_7)/4$

Interaction A&B: $\quad E_{AB} \quad = (y_1+y_4+y_5+y_8)/4 - (y_2+y_3+y_6+y_7)/4$

Interaction A&C: $\quad E_{AC} \quad = (y_1+y_3+y_6+y_8)/4 - (y_2+y_4+y_5+y_7)/4$

Interaction B&C:　　E_{BC}　$= \underline{(y_1+y_2+y_7+y_8)}/4 - \underline{(y_3+y_4+y_5+y_6)}/4$

Interaction A,B,&C:　E_{ABC}　$= \underline{(y_2+y_3+y_5+y_8)}/4 - \underline{(y_1+y_4+y_6+y_7)}/4$

The calculated effects will tell the contribution of each factor and the combinations on the changes, where the higher number represents higher effect. The mathematical model, which represents the result can be written as followed.

$$Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{123}ABC + c$$

$$\text{Where } b_0 = (1/8)(y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8)$$

$$b_x = E_x/2$$
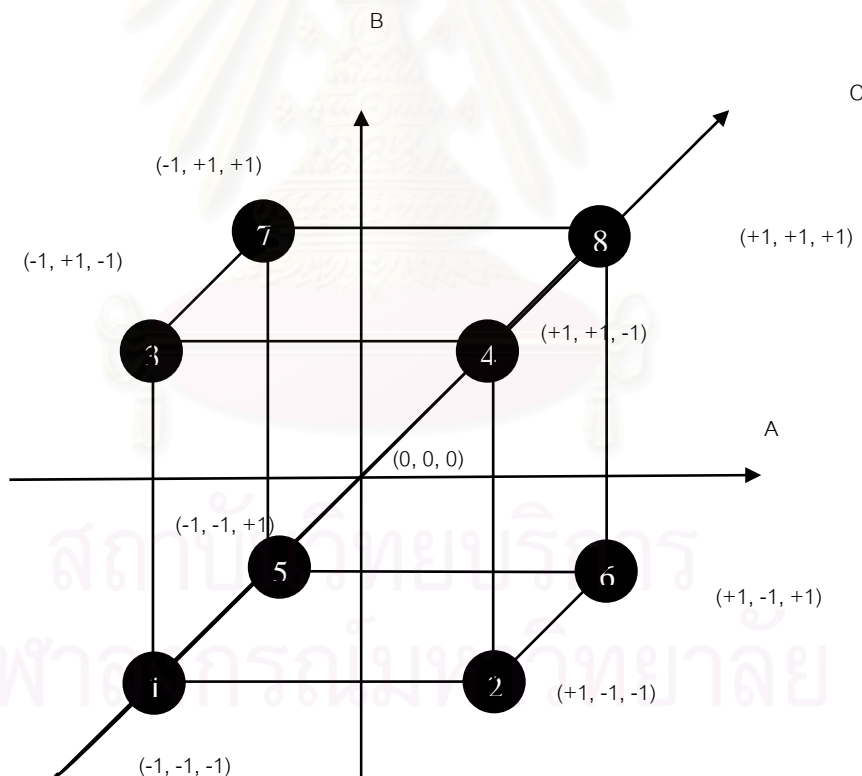
Figure 2.6 Geometric representation of 2^3 factorial design

The 2^3 factorial design was chosen in this experiment because there were limited knowledge on this recovery, therefore, the design with less experiment like

fractional design should not be chosen. The 2^3 factorial design's result will give based on linear assumption, which is preferred for the study of short interval of factors being study. And the chosen of number of factors being study was based on the "parsimony concept" where less is better.

2.2 Literatures Review

Pichainarong (2002) observed the precipitation of lignin from Eucalyptus based black liquor by lowering of pH of the solution using Sulphuric acid. The pH was lower to 5, 4, 3, 2, and 1.5. It was found that pH 3 is the optimum pH for lignin precipitation and the recovery of 93.51% was achieved.

Mussatto et al (2007) studied the recovery of lignin from brewer's spent grain black liquor by acidification using Sulfuric acid. In the study, ten pH values were varied from 12.56 to 2.15. It was found that the removal of lignin reached 81.43% at most.

Avsar et al. (2007) studied the treatment of rose processing wastewater using electrocoagulation with iron electrodes and compare it with the classical chemical (CC) and Fenton application (FA) processes by determining the chemical oxygen demand (COD) and dissolved solids contents before and after treatment. As a result, it was found that for CC process using $Al_2(SO_4)_3$ 18H2O, maximum COD and turbidity removals were obtained as 29.2% and 43.5%, respectively. In FA experiments, the process was tested both classical fenton application (CFA) and graded fenton application (GFA) processes as two stages. The GFA gave better results than the CFA. COD and turbidity removal efficiencies were 72.5% and 74.2% for the GFA, 65.7% and 67.5% for the CFA process, respectively. As for the EC process, shorter reaction time and the highest COD and turbidity removal rates were obtained. The highest COD and turbidity removals were 79.8% and 81.4% and the optimum reaction time was 20 min. When they are compared, the sequence of treatment methods is EC >GFA>CFA> CC, respectively, for COD and turbidity removals.

Teangvannakant (2003) studied the removal of reactive dye by using electrocoagulation process and chemical coagulation. It was found that the optimal condition for reactive dye removal is at voltage of 30 Volts, reaction time of 1.5 hours, starting pH of 5.85, , and iron electrode size at least 3x6.5 cm at conductivity of 7.2 ms/cm . When compare result of electrocoagulation to chemical coagulation, it was found that electrocoagulation alone had higher efficiency, 97% removal while chemical coagulation can remove only 28.35%.

Sinsomboon (2006) studied the removal of dye by electrochemical process using aluminum and iron. Experiments were done in batch mode to determine the optimum treatment condition by vary current density, reaction time, and concentration of dye using 2^3 factorial design with 5 center points.   The factors being varied were summarized as followed.

Factors	Levels				
1. Current density (mA/cm^2)	0.86	5	10	15	29.14
2. Time (min.)	3.33	5	10	15	17.07
3. Dye concentration, mg/L	18.95	50	125	200	231.05

It was found that the optimal condition for color removal is at current density of 29.14 mA/cm^2, time of 10 min., and dye concentration of 125 mg/L. It was also found that at this condition, the expense is the highest where aluminum electrode cost more than iron electrode, 166.32 baht/m^3 and 161.92 baht/m^3. When compare the performance of aluminum and iron electrodes, it was found that both type of electrode can remove color and COD effectively. However, water treated by iron electrode will have sometime black or green color due to the color of Fe ions produced. Another difference of aluminum and iron electrode is the settling time of solids. The settling time of iron electrode will be faster than aluminum electrode due to the heavier molecular mass of iron, 55.847, over aluminum, 26.981.

CHAPTER III

EXPERIMENT

The experiment was done at the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM) Laboratory, Chulalongkorn University with the equipments and chemicals supported by the laboratory.

3.1 Experimental Plan

The experiment was done to find the percent removal of lignin from black liquor after pH adjustments, which were done in 3 levels, using electrochemical process. In this study, two types of electrodes, a pair of aluminum and a pair of iron electrodes were used. The 2^3 factorial experimental design or design of experiment was used to understand and quantify the relationship of factors affecting lignin recovery and to explain the separation process.

3.2 Apparatus and Chemical Use

Apparatus

- Laboratory power supply: GW Model GPR-6060D
- Electrodes: aluminum and iron electrodes with 5 cm x 2.5 cm reaction dimension. With two sides of reaction that occurred, the reactive surface of an electrode will be 25 cm^2. The pictures of electrodes are shown in Figure 3.1 and the experimental set up is shown in Figure 3.2.
- UV spectrophotometer: Thermo Electron Corporation
- Centrifuge: BOECO Germany Model C-28
- Magnetic stirrer: LABINCO
- pH meter: SCHOTT Instrument Model B052907 034

Chemical

- Sulfuric acid: Merck 95-97%

a)

b)

Figure 3.1 a) Aluminum electordes b) Iron electrodes
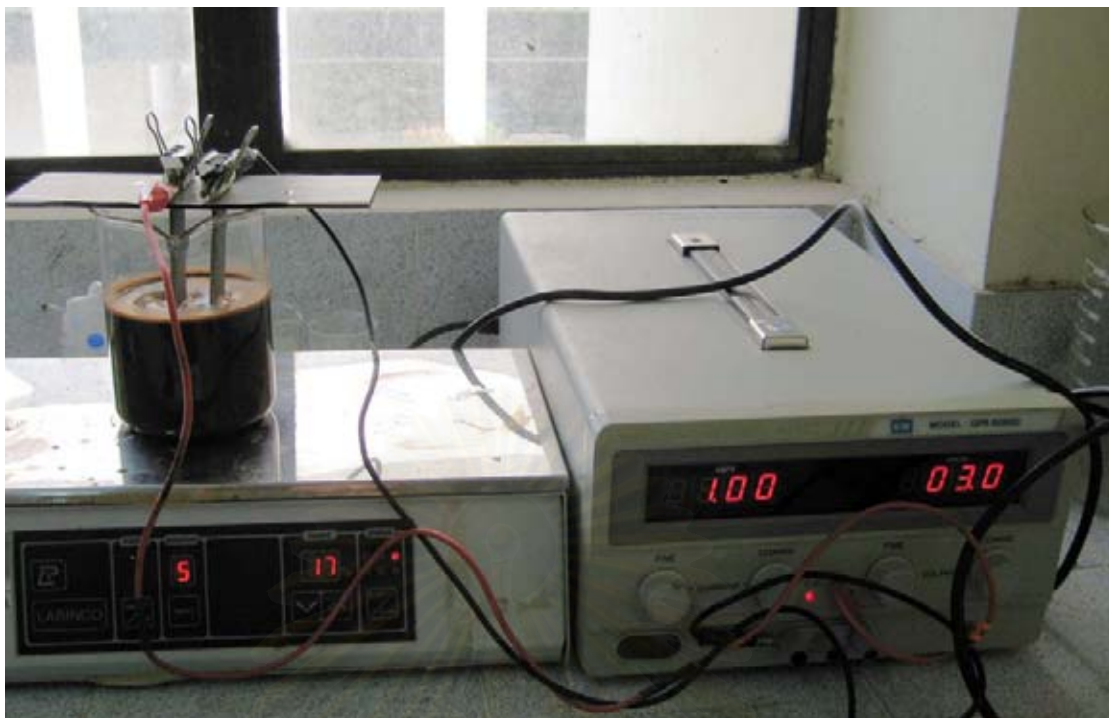
Figure 3.2 Experimental set up

3.3 Variables in the Study

After researches and preliminary tests, it was found that the factors that should have the most impact on lignin precipitation were current density, time, and initial solids content. The controlled variables were type of electrodes, aluminum and iron, and adjusted initial pH of black liquor prior to electrochemical process, which were 8, 7, and 6.

3.3.1 Current Density

According to Faraday's law of electrolysis, the mass of a substance produced at an electrode during electrolysis is directly proportional to the number of electrons (the quantity of electricity) transferred at that electrode. Therefore, it was expected that higher in current density will result in higher precipitation. The current density was varied into 2 levels and each level was put in coded value. Current density of each type of electrode was intended to be the same. However, after preliminary test, it was found that the suitable range of current density of aluminum and iron electrodes were different.

Aluminum Electrodes:

Level   -1   represents current density of 4 mA/cm^2

Level   +1   represents current density of 8 mA/cm^2

Iron Electrodes:

Level   -1   represents current density of 2 mA/cm^2

Level   +1   represents current density of 12 mA/cm^2

3.3.2 Time

As the reaction time increases, chance of ions produce from electrode and lignin precipitation to occur were expected to increase as well. The levels of reaction being studied were varied into 2 levels, which were the same for both electrodes.

Level   -1   represents time of 5 min.

Level   +1   represents time of 15 min.

3.3.3 Initial Solids Content

The reaction that occurs from the removal process is partly controlled by the initial solids content of solution, which is the main substance that will react with the metal ions produced. The initial solids content were varied into 2 levels. It was the same for both aluminum and iron electrodes.

Level   -1   represents solids content of 10%

Level   +1   represents solids content of 15.3 %

Summary of factors at different level can be seen in Table 3.1 for aluminum electrodes and Table 3.2 for iron electrodes. The geometric representation of 2^3 factorial design for aluminum electrodes is shown in Figure 3.3 and for iron electrodes in Figure 3.4.

Table 3.1 Summary of levels of factors for aluminum electrodes

Factors	Values	
	Level -1	Level +1
Current Density, mA/cm^2	4	8
Time, min.	5	15
Initial solids content, %	10	15.3
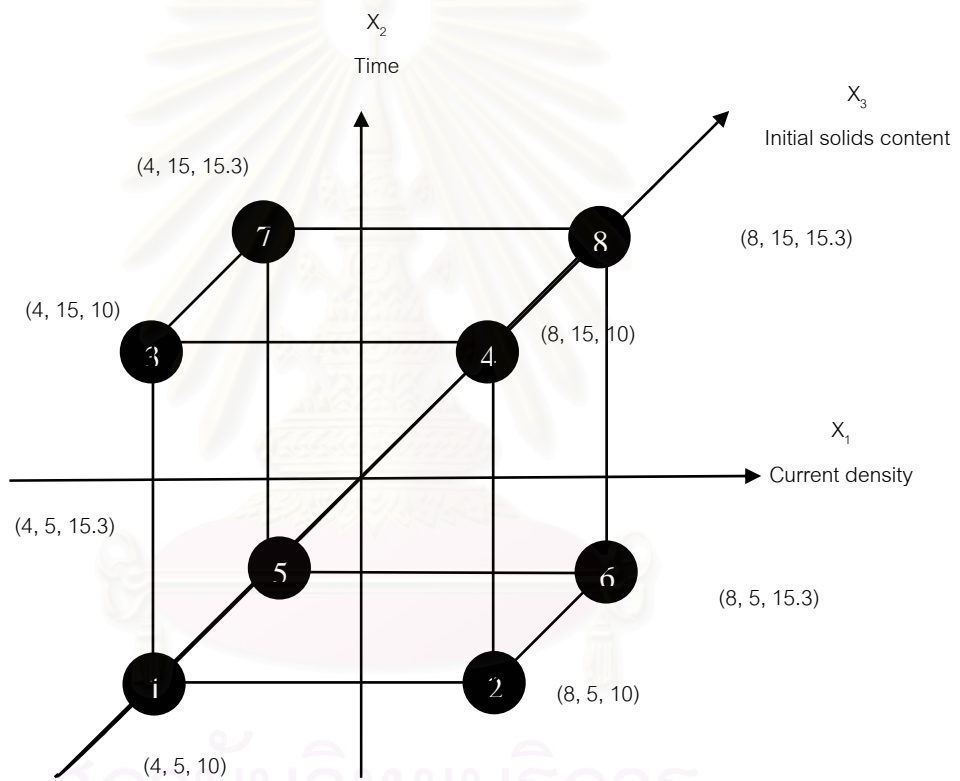
Figure 3.3 Geometric representation of 2^3 factorial design of aluminum electrodes

Table 3.2 Summary of levels of factors for iron electrodes

Factors	Values	
	Level -1	Level +1
Current Density, mA/cm^2	2	12
Time, min.	5	15
Initial solids content, %	10	15.3
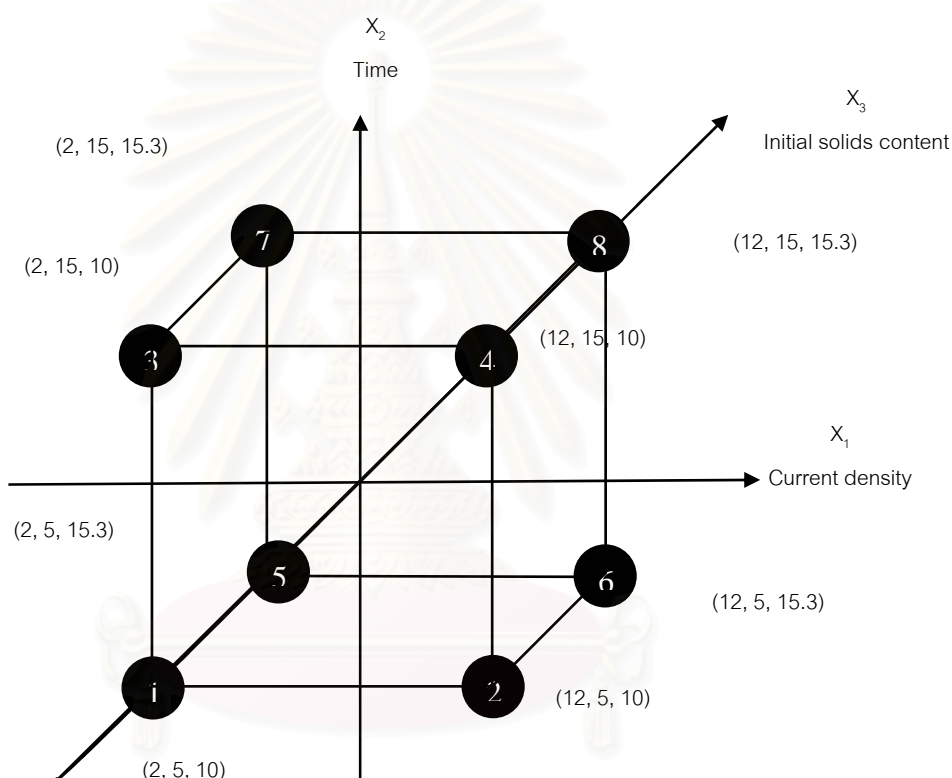
Figure 3.4 Geometric representation of 2^3 factorial design of iron electrodes

3.4 Methodology

3.4.1 Preliminary Test

Preliminary test was done to study and find the appropriate ranges of factors, current density and reaction time, studied in the experiment for both aluminum and iron electrodes. The preliminary study was done at the initial pH of 7 where pH of black

liquor was lower from about 12.5 to 7 using sulfuric acid and at the original initial solids content of 15.3%. Conditions being studied and their results are summarized in Table 3.3 for both aluminum and iron electrode.

Table 3.3 Levels of factors study in preliminary test

Experiment	Current density, mA/cm^2	Time, min.
1	2	5
2	2	15
3	4	5
4	4	15
5	4	30
6	8	5
7	8	15
8	8	30
9	12	5
10	12	15
11	12	30

3.4.2 Preparation of Black Liquor

<u>1. Initial Solids Adjustment</u>

The original initial solids of black liquor was measure by oven dry at 105 ºC. Then it was adjusted to the desire levels by oven dry or addition of distill water.

<u>2. pH Adjustment of Black Liquor</u>

The pH of black liquor was adjusted to different levels; 8, 7, and 6, prior to the electrochemical process. The pH adjustment was done by the addition of sulfuric acid with magnetic stirrer as mixing aid.

3.4.3 Precipitation by Electrochemical Process

1. Electrochemical Process

After pH was adjusted, black liquor will be brought to electrochemical process. The electrochemical process can be divided into two main processes according to the type of electrode used, which were aluminum and iron electrodes. Each type of electrode was having different combination of levels of variable for the study. Black liquor samples of 350 ml in 600 ml beaker were used. The magnetic stirrer was used to aid the mixing during the process. The total amount of 144 experiments were done. The conditions and replication of each electrode are shown in Table 3.4 and Table 3.5.

2. Centrifugation

After electrochemical process, 40 ml of sample was transferred to the centrifugal tube and centrifuged to separate the liquid and solids part. The centrifugation was done at 3000 rpm for 20 min.

3. Lignin Concentration Measurement

After centrifugation, 100 µl of supernatant was removed from the centrifugation tube and diluted in 100 ml flask with distilled water. Concentration of lignin can be measured using UV spectrophotometer at wavelength of 280 nm. The result can be converted to lignin concentration using lignin calibration curve, which prepared from standard lignin powder.

3.4.4 Model Analysis

The analyses of data were done and the 2^3 factorial design was used to describe the behavior of factors on the separation and to create model. The over all experimental plan is shown in Figure 3.5.

Table 3.4 Levels of variables studied for aluminum electrodes

Experiment	Coded Values of the Variables			Replications
	Current density	Time	Initial Solids Content	
pH8				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
pH 7				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
pH 6				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
			Total	72

Table 3.5 Levels of variables studied for Iron electrode

Experiment	Coded Values of the Variables			Replications
	Current density	Time	Initial Solids Content	
pH8				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
pH 7				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
pH 6				
1	-1	-1	-1	3
2	+1	-1	-1	3
3	-1	+1	-1	3
4	+1	+1	-1	3
5	-1	-1	+1	3
6	+1	-1	+1	3
7	-1	+1	+1	3
8	+1	+1	+1	3
			Total	72

Figure 3.5 Overall experimental plan

CHAPTER IV

RESULTS AND DISCUSSION

In this experiment, the factors affecting lignin recovery were studied. Current density, time, and initial solids content were varied into two levels with two types of electrodes, aluminum and iron. Analyses of individual effects and interaction effects for factors were studied using design of experiment and the models for the recovery were formed. Each experimental condition was done with three replications.

4.1 Preliminary Test

Preliminary test was done to study and find the appropriate ranges of factors, current density and reaction time, studied in the experiment for both aluminum and iron electrodes. Preliminary test results are summarized in Table 4.1 for aluminum electrodes and Table 4.2 for iron electrodes. From the preliminary test, aluminum and iron electrodes reacted differently on lignin recovery at various current densities. For aluminum, the recovery occurred at 4 mA/cm^2 and at 8 mA/cm^2 where positive recoveries were found. At 12 mA/cm^2, it did not give positive result and the higher current density used will aid the increasing of amount of foam created, which interrupted the circuit and recovery process. Therefore, the current densities for aluminum electrodes were chosen to be 4 mA/cm^2 for lower level (-1) and 8 mA/cm^2 for higher level (+1). For iron electrodes, the recovery occurred in wide range, only one condition was having small negative result. This was possibly an experimental error, since there was no other condition resulting in negative recovery. Therefore, current densities of iron electrode were chosen to be 2 mA/cm^2 for low level (-1) and 12 mA/cm^2 for high level (+1).

For the reaction time, it was found that at higher current density with higher reaction time, there will be foam created especially for aluminum electrode. The reaction time of 30 min. gave a lot of foam, which in some combination (with * sign) foam was

Table 4.1 Preliminary test result using aluminum electrodes

Experiment	Current density, mA/cm^2	Time, min.	Lignin recovery, %	Additional lignin recovery by electrochemical process, %
1	2	5	64.34	-0.27
2	2	15	63.75	-0.87
3	4	5	67.63	3.02
4	4	15	63.89	-0.72
5	4	30	62.10	-2.52
6	8	5	65.09	0.47
7	8	15	64.57	-0.05
8	8	30	60.76	-3.86
9	12	5	65.84	1.22
10	12	15	62.18	-2.44*
11	12	30	60.23	-4.38*

Table 4.2 Preliminary test using iron electrodes

Experiment	Current density, mA/cm^2	Time, min.	Lignin recovery, %	Additional lignin recovery by electrochemical process, %
1	2	5	64.91	0.30
2	2	15	64.24	-0.37
3	4	5	66.33	1.71
4	4	15	66.18	1.56
5	4	30	67.30	2.68
6	8	5	67.22	2.61
7	8	15	67.89	3.28
8	8	30	66.55	1.94
9	12	5	67.74	3.13
10	12	15	65.06	0.45
11	12	30	66.03	1.41*

over flow and was disturbing the circuit. Some of the foam had to be removed, therefore, the results of these tests might involved some error due to removal of sample and disturbance to the circuit that sometime the tests had to end sooner than expected. Together with the fact that in most cases, shorter reaction time seemed to give better result, thus, consume less electricity, therefore reaction time of 5 and 15 min. were chosen for both electrodes.

For initial solids content, the original initial solids content, 15.3%, was chosen to be +1 level because we wanted to try the direct use of black liquor from the pulping process without any treatment. The lower level, -1, of initial solids content was chosen to be 10%, since dilution by distilled water consume less energy than drying to increase the solids content of black liquor and 10% should be a suitable range that is not too wide or too narrow for the study. Another reason involve drying of black liquor was the chemical changes that might occur during heating process. Therefore initial solids content of 10% and 15.3% were chosen. The additional lignin recovery by electrochemical process can be calculated by compare the result after electrochemical process with recovery from acidification alone. Background values and the recovery from acidification alone can be seen in Appendix B.

4.2 Acidification and Electrochemical Process

In the study, prior to the electrochemical process, pH of black liquor was adjusted from about 12.5 to 8, 7, and 6. After pH adjustment, color of black liquor was changed from very dark brown to lighter brown where the color of black liquors of different adjusted pH were quite the same. Figure 4.1 shows black liquor before and after pH adjustment. Then the pH-adjusted black liquor was used in electrochemical process. With aluminum electrodes, there was light and bulky foam created during the electrochemical process. This is the result from soap-like nature of black liquor, which is the result of fatty acid and NaOH contained in black liquor that are the main components of soap (The Soap and Detergent Association, [online], Chao, [online]). Eucalyptus wood contains about 22 mg of fatty acid in 100 g. of wood (Gutierrez, 1998) while sodium hydroxide is a main digesting chemical used in pulping process. This foam was

Figure 4.1 Original black liquor (left) and black liquor after pH adjustment (right)

associated with higher current density , which give rise to hydrogen gas production during the electrochemical process (Adhoum and Monster, 2004, Ugurlu et al, 2008). The picture of foam created when use aluminum as electrode is shown in Figure 4.2. However, with iron electrodes, foam also created but in slower speed.

Figure 4.2 Foam associated with aluminum electrodes during electrochemical process

For the electrodes used in the experiments, both aluminum and iron electrodes, after electrochemical process, we can see small bumps and scratches resulting from the losses of the metal from the electrode's surface. However, loses of the metal was very little on the surface of the electrodes and they can be continuously used throughout the experiments.

Black liquor after electrochemical process will be transferred to centrifugal tube and centrifuged at 3000 rpm for 20 min. to aid the precipitation. After precipitation, the separation of solids and liquid can be seen clearly as shown in Figure 4.3. Then the liquid part was used for lignin concentration analysis using spectrophotometer at wavelength of 280 nm. Lignin concentration before and after treatment process were used to determine lignin recovery percentage, which was done based on mass balance concept. However, lignin recovery from this process was surely not pure, it will surely at least have the mixture of the metal used. Further purification would needed according to the application used. It can recognized that the color of the solution and the precipitated solid using iron electrodes had darker brown color than the one of aluminum electrodes, which was the result from the color of iron ions.

Figure 4.3 Black liquor samples after centrifugation

4.2.1 Aluminum Electrodes

4.2.1.1 Initial pH of 8

The result of lignin recovery from black liquor using aluminum electrodes with adjusted pH of 8 prior to electrochemical process together with coefficient of variation (CV) of the results are shown in Table 4.3. The geometrical representation of the test result of aluminum electrodes at pH 8 is shown in Figure 4.4.

Table 4.3 Lignin recovery at initial pH 8 using aluminum electrodes

Experiment	Current density	Time	Initial solids content	Final pH	Lignin recovery, %	Additional Lignin recovery by electrochemical process, %	CV*, %
1.	-1	-1	-1	8.17	22.29	-7.08	2.03
2.	1	-1	-1	8.20	20.05	-9.33	1.08
3.	-1	1	-1	8.31	15.20	-14.18	2.12
4.	1	1	-1	8.53	17.50	-11.88	0.63
5.	-1	-1	1	8.12	61.76	-1.16	2.32
6.	1	-1	1	8.15	60.89	-2.04	2.73
7.	-1	1	1	8.30	61.94	-0.99	4.34
8.	1	1	1	8.39	61.81	-1.11	5.09

* CV = standard deviation / mean

From the result, it can be seen that at pH 8, lignin recoveries were not accomplished. The negative recovery vales indicate that amount of precipitated lignin after electrochemical process was less than those before the process, which was a result of pH adjustment alone. This may due to several possible reasons. At pH 8, ions were mainly existed in negative form, OH^-, which was not enough for aiding the precipitation. The aluminum ions that form may not be in a suitable form or are not enough for destabilization or neutralize negative charge in the system, since the monomeric and polymeric hydroxo-complexes formed
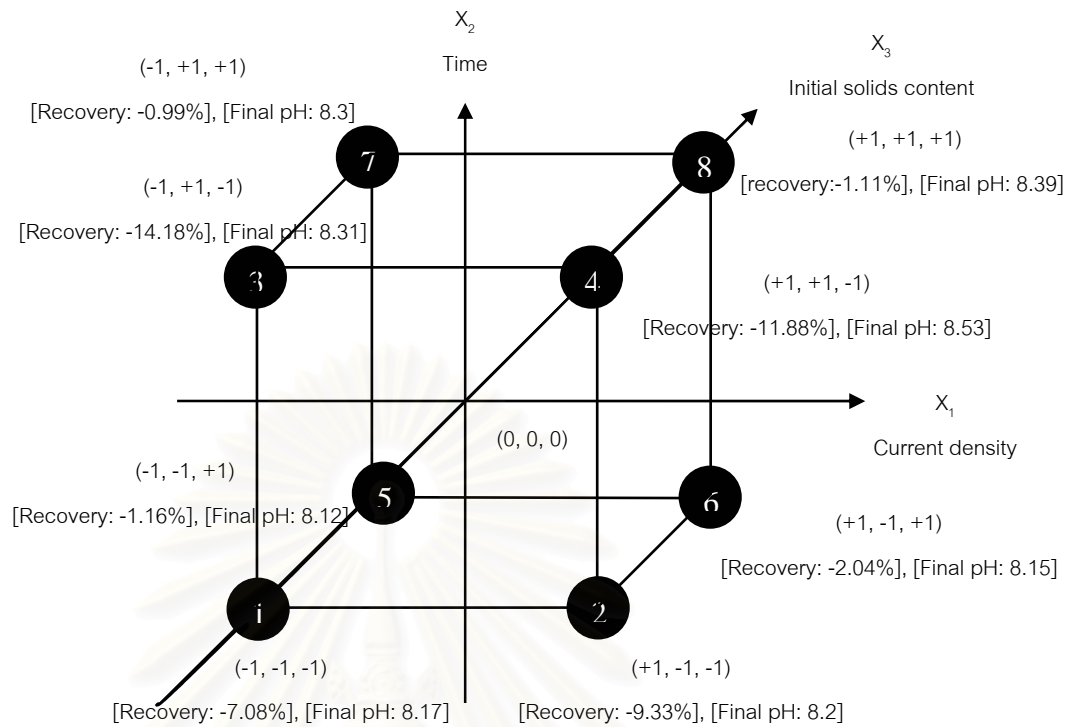
Figure 4.4 Geometrical representation of the test result of aluminum electrodes at pH 8

will depend on the pH range(Ugurlu et al, 2008). At high pH, solubility of aluminum hydroxide is increased and lead to the formation of soluble AlO_2^- (Adhoum and Monser, 2004), which did not aid the precipitation process. Also, after the electrochemical process, pH increased due to OH^- oxidation and reduction reaction that occur.

It can be seen that high level of current density (compare point 8 to 7, 4 to 3, 6 to 5, and 2 to 1) and reaction time (compare point 7 to 5, 3 to 1, 8 to 6, and 4 to 2) will resulted in higher final pH. This resulted in higher negative charge, thus may incur resuspension of destabilized lignin in the system, which may make the recovery to be negative. It also can be seen that at higher level of initial solids content, the negative recovery was lower than the lower level of initial solids content.

4.2.1.2 Initial pH of 7

The result of lignin recovery at initial pH 7 using aluminum electrodes is shown in Table 4.4 and the geometric representation of the test result of aluminum electrode at pH 7 is shown in Figure 4.5. From the experiment, the recovery was mostly negative. The positive recoveries occurred in some condition at high initial solids content where it reached highest lignin recovery of 65.88%, which is the result of electrochemical process 1.26%, at high level of current density and low level of time (experiment 6). This result as well as for the result of pH 8 indicated that higher level of initial solids is better for lignin recovery. This may be because higher solids, which should associated with higher lignin content, provide higher level of target for the reaction and precipitation to occur. However, the positive and negative recoveries indicated that at pH 7, the condition stills not wholly applicable for electrochemical process.

Table 4.4 Lignin recovery at initial pH 7 using aluminum electrodes

Experi-ment	Current density	Time	Initial solids content	Final pH	Lignin recovery , %	Additional Lignin recovery by electrochemical process, %	CV, %
1.	-1	-1	-1	7.31	37.79	-4.76	3.79
2.	1	-1	-1	7.48	38.25	-4.31	4.42
3.	-1	1	-1	7.66	40.78	-1.78	2.66
4.	1	1	-1	7.73	31.04	-11.52	2.78
5.	-1	-1	1	7.25	65.05	0.44	2.13
6.	1	-1	1	7.41	65.88	1.26	8.43
7.	-1	1	1	7.58	64.61	-0.01	2.60
8.	1	1	1	7.87	63.38	-1.23	1.63
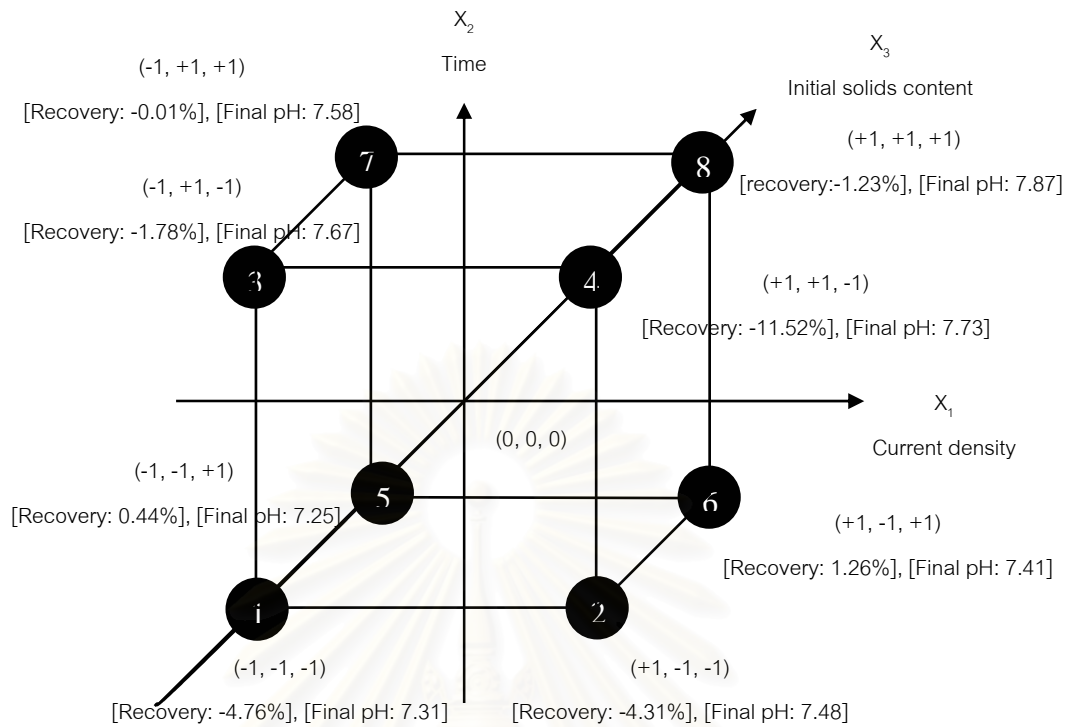
Figure 4.5 Geometric representation of the test result of aluminum electrodes at pH 7

It can be seen that higher in current density and time gave higher final pH as in pH 8 but does not always give higher recovery value as predicted. For examples, at higher levels of current density (compare point 8 to 7 and 4 to 3) give lower recovery than lower levels of current density. Higher levels of time (compare point 3 to 1, 4 to 2, 7 to 5, and 8 to 6) give less recovery than the lower levels time. The higher level of final pH that associated with high current density and time were due to the production of OH^- that was produced as a result of oxidation and reduction reaction that took place in the system as current density and time increased. As can be seen in equations below, which shows the reaction occurred for aluminum electrodes.

Oxidation reaction at anode (Biwyk, 1991)

$$2\ Al_{(s)} \quad \longrightarrow \quad 2Al^{3+}_{(aq)} + 6\ e^- \qquad (4.1)$$

$$2H_2O_{(l)} \quad \longrightarrow \quad O_{2(g)} + H^+_{(aq)} + 4e^- \qquad (4.2)$$
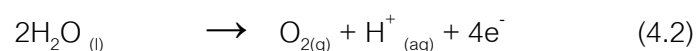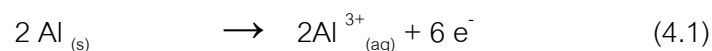
Reduction reaction at cathode

$$2H_2O_{(l)} + 2e^- \quad \longrightarrow \quad H_{2(g)} + 2OH^-_{(aq)} \qquad (4.3)$$

Oxidation reduction reaction

$$2Al_{(s)} + 6H_2O_{(l)} \longrightarrow 3H_{2(g)} + 2Al(OH)_{3(s)} + 6OH^- \qquad (4.4)$$
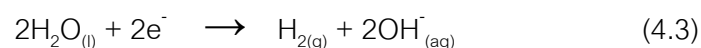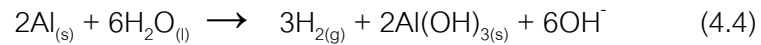
4.2.1.3 Initial pH of 6

At pH 6, lignin recovery is positive for all conditions. The highest recovery is at high level of current density, low level of time, and high level of initial solids content. The recovery reached 82.86% where 14.89% is the result of electrochemical process. The lowest recovery is at low current density, low time, and low initial solids content where the over all recovery is 47.59% and is the result of electrochemical process of 1.3%. This precipitation is the result of monomeric and polymeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH_2)^{4+}$, $Al(OH)_4^-$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ produced and perform charge neutralization with negative colloid in the system, and $Al(OH)_3$, which is an amorphous and gelatinous form of aluminum complex that will enmeshes colloidal particles in "sweep floc" mechanism (Gurses et al, 2002). However, form of these complexes will depend on pH of solution (Gurses et al, 2002). The results of lignin recoveries at initial pH of 6 using aluminum electrodes and the geometric representation of the test result of aluminum electrodes at pH 6 are shown in Table 4.5 and Figure 4.6.

From the result, high level of current density and time also resulted in higher level of final pH, which agreed to both pH 8 and 7. Also, higher current density seems to give higher recovery values (compare point 8 to 7, 6 to 5, and 2 to 1). Result of time cannot be concluded by comparing each point because higher level of time gave both higher and lower levels of lignin recovery. The higher initial solids content gave better recovery (compare point 5 to1, 6 to 2, 7 to 3, and 8 to 4), which confirm the results in both pH 8 and 7.

Table 4.5 Lignin recovery at initial pH 6 using aluminum electrodes

| Experiment	Current density	Time	Initial solids content	Final pH	Lignin recovery, %	Additional Lignin recovery by electrochemical process, %	CV, %
1.	-1	-1	-1	6.44	47.59	1.30	1.20
2.	1	-1	-1	6.64	52.47	6.18	4.07
3.	-1	1	-1	6.89	52.10	5.81	4.43
4.	1	1	-1	6.86	50.66	4.37	1.85
5.	-1	-1	1	6.35	75.82	7.85	1.35
6.	1	-1	1	6.68	82.86	14.89	3.42
7.	-1	1	1	6.64	76.38	8.41	0.84
8.	1	1	1	7.19	80.80	12.83	7.87
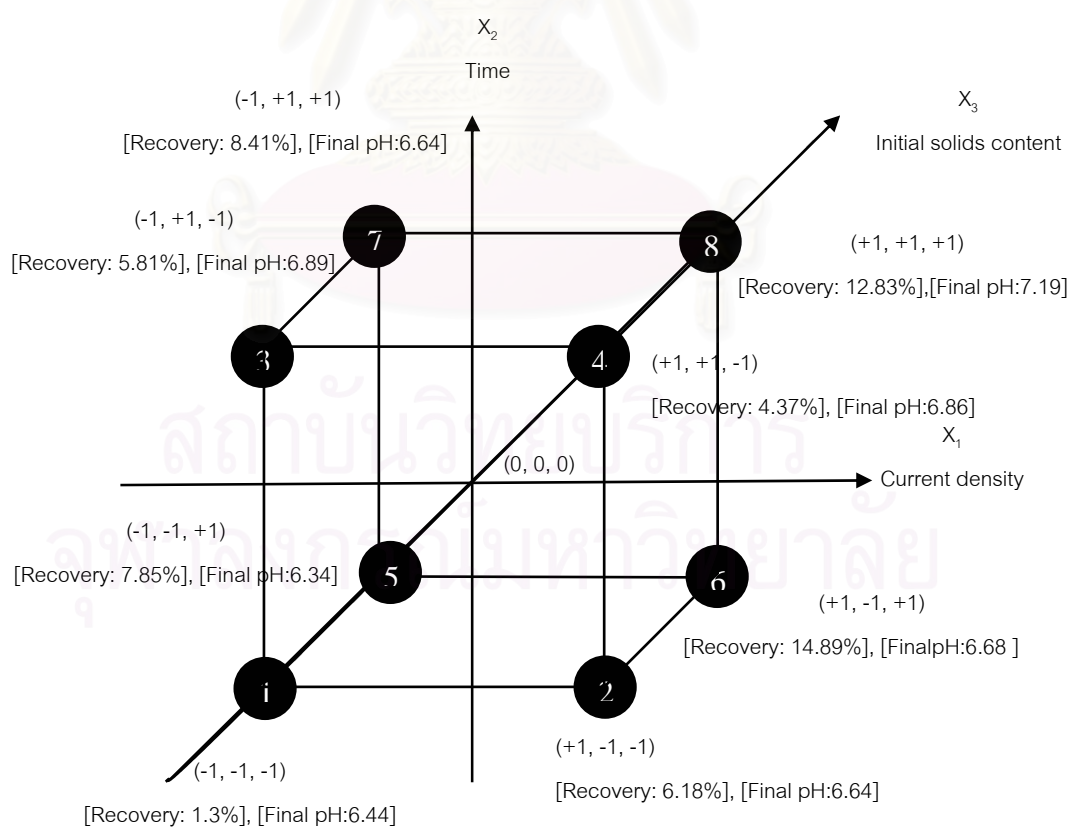
Figure 4.6 Geometric representation of the test result of aluminum electrodes at pH 6

4.2.2 Iron Electrodes

4.2.2.1 Initial pH of 8

The result of lignin recovery from black liquor using iron electrodes with adjusted pH of 8 prior to electrochemical process together with coefficient of variation (CV) of the results are shown in Table 4.6 and the geometric representation of the test result of iron electrodes at pH 8 is shown in Figure 4.7. From the test, it was found that at pH 8, recovery cannot be accomplished as for aluminum electrodes and their reasons should be similar. It can be seen that final pH of lower initial solids content seems to be higher and the resuspension seems to occur more in lower solids content. It can also be seen that more current density and less time gave less resuspension to the systems.

Table 4.6 Lignin recovery at initial pH 8 using iron electrodes

Experi-ment	Current density	Time	Initial solids content	Final pH	Lignin recovery, %	Additional Lignin recovery by electrochemical process, %	CV, %
1.	-1	-1	-1	8.17	26.44	-2.94	1.18
2.	1	-1	-1	8.35	25.64	-3.73	3.26
3.	-1	1	-1	8.30	16.81	-12.56	2.62
4.	1	1	-1	8.67	22.26	-7.11	2.25
5.	-1	-1	1	8.22	60.38	-2.55	3.00
6.	1	-1	1	8.30	62.33	-0.60	0.86
7.	-1	1	1	8.25	55.96	-6.97	0.95
8.	1	1	1	8.43	59.65	-3.28	3.52
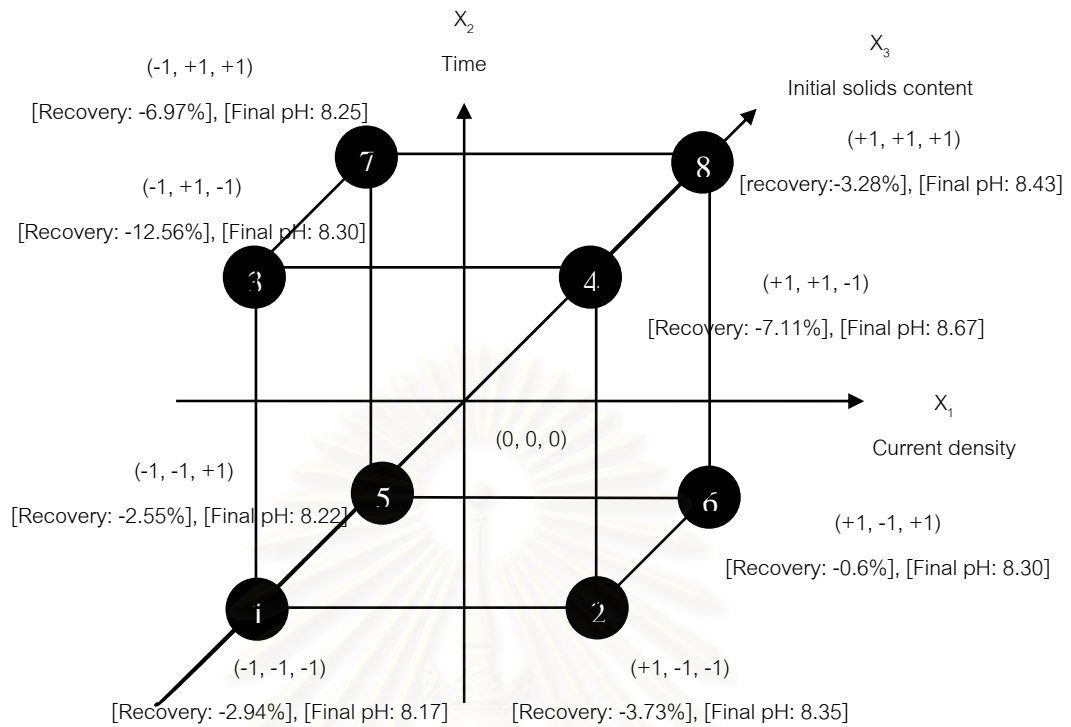
Figure 4.7 Geometric representation of the test result of iron electrodes at pH 8

4.2.2.2 Initial pH of 7

From the result, it can be seen clearly that lignin recovery of lower level of initial solids content give lower recovery result, where in this case the negative values were obtained, it also associated with higher final pH (compare point 1 to 5, 2 to 6, 3 to 7, and 4 to 8). At the higher level of initial solids, the recoveries were found positive. The highest lignin recovery occurred at point 8, which the recovery is 70.01% and 5.4% is the result of electrochemical process, where current density, time, and initial solids content were in high level. The lowest recovery is 65.05% or 0.44% as a result of electrochemical process, which occurred at low current density, high time, and high initial solids content.

At higher current density and time, final pH was higher as well. At high current density, lignin recovery will be higher when initial solids content is also high (compare point 8 to 7 and 6 to 5) but at lower solids content, it went other way (compare point 2 to 1 and 4 to 3). For time, higher level gave higher final pH and seemed to give higher recovery as well. This increased in pH was as a

result of OH$^-$ production in oxidation reduction reaction that occured in the system as shown below.

Oxidation at anode: (Biwyk, 1991)
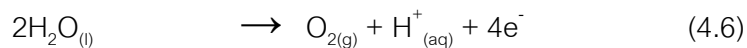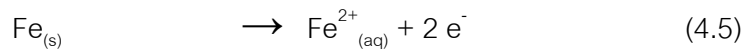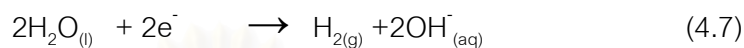
$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\ e^- \tag{4.5}$$

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + H^+_{(aq)} + 4e^- \tag{4.6}$$

Reduction at cathode

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{4.7}$$

Oxidation and reduction reaction

$$Fe_{(s)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + Fe(OH)_{2(s)}^- + 2OH^-_{(aq)} \tag{4.8}$$
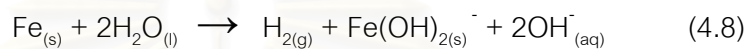
The result of lignin recovery at initial pH 7 using iron electrodes is shown in Table 4.7 and the geometric representation of the test result of iron electrodes at pH 7 is shown in Figure 4.8.

Table 4.7 Lignin recovery at initial pH 7 using iron electrodes

Experiment	Current density	Time	Initial solids content	Final pH	Lignin recovery, %	Additional Lignin recovery by electrochemical process, %	CV, %
1.	-1	-1	-1	7.33	38.67	-3.88	4.21
2.	1	-1	-1	7.55	37.99	-4.56	8.39
3.	-1	1	-1	7.58	40.18	-2.38	5.43
4.	1	1	-1	8.23	38.73	-3.82	5.89
5.	-1	-1	1	7.28	65.53	0.91	6.48
6.	1	-1	1	7.47	69.07	4.45	5.05
7.	-1	1	1	7.49	65.05	0.44	5.22
8.	1	1	1	7.97	70.01	5.40	3.50
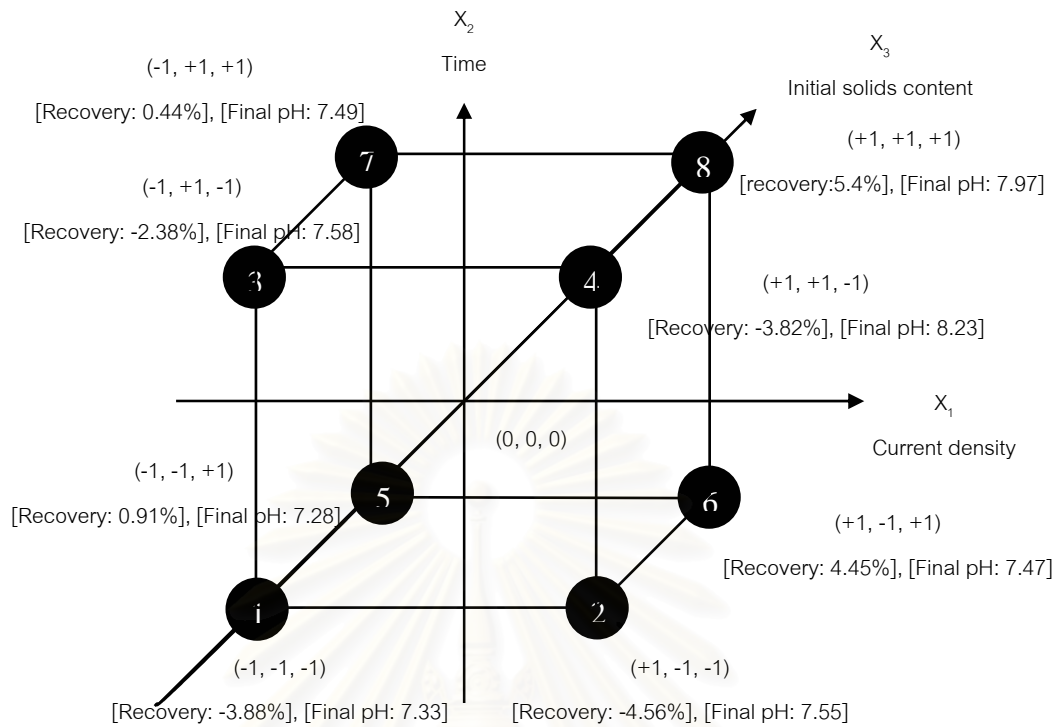
Figure 4.8 Geometric representation of the test result of iron electrodes at pH 7

4.2.2.3 Initial pH of 6

At initial pH 6 of iron electrodes, recoveries were all positive. The highest lignin recovery was 78%, which was the result of electrochemical process 10.03%. The condition that gave the best result was at high level of current density, time, and initial solids content. The lowest lignin recovery was 47.65% where 1.36% was the result of electrochemical process. It occurred at low level of current density, time, and initial solids content. This recovery was the result of ferric ions electrogenerated, which may form monomeric ions, ferric hydroxo complex with hydroxide ions and polymeric species such ac $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH_2^{+}$, $Fe(H_2O)_4OH_2^{+}$, $Fe_2(H_2O)_8OH_2^{4+}$, and $Fe_2(H_2O)_6OH_4^{2+}$, which will depend on the pH range(Gurses et al, 2002). It can be seen clearly that at higher level of initial solids content, lignin recovery will be higher too. High current density resulted in higher recovery and final pH than low current density. High level of time resulted in higher recovery and final pH than low level of time. The result of lignin recovery at initial pH 6 using iron electrodes is shown in Table

4.8 and the geometric representation of the test result of iron electrodes at pH 6 is shown in Figure 4.9.

Table 4.8 Lignin recovery at initial pH 6 using iron electrodes

Experi-ment	Current density	Time	Initial solids content	Final pH	Lignin recovery, %	Additional Lignin recovery by electrochemical process, %	CV, %
1.	-1	-1	-1	6.39	47.65	1.36	2.33
2.	1	-1	-1	6.99	48.95	2.66	0.19
3.	-1	1	-1	6.72	49.83	3.54	1.19
4.	1	1	-1	8.32	52.56	6.27	1.18
5.	-1	-1	1	6.28	75.04	7.08	0.82
6.	1	-1	1	6.56	77.54	9.57	0.50
7.	-1	1	1	6.43	76.38	8.41	5.47
8.	1	1	1	7.44	78.00	10.03	1.63

4.3 Model Analysis

From the result obtained, main effects, which are the average of effects of each factor, and interaction effects, which are the average result of more than one factor acting together can be calculated. They will show both magnitude and direction of the factors corresponded to the test result and the model will be constructed.

4.3.1 Aluminum Electrodes

4.3.1.1 Initial pH of 8

The summary of result of lignin recovery using aluminum electrode at pH 8 can be seen in Table 4.9. This result will be used to calculate both main and interaction effect of factors involving the recovery.
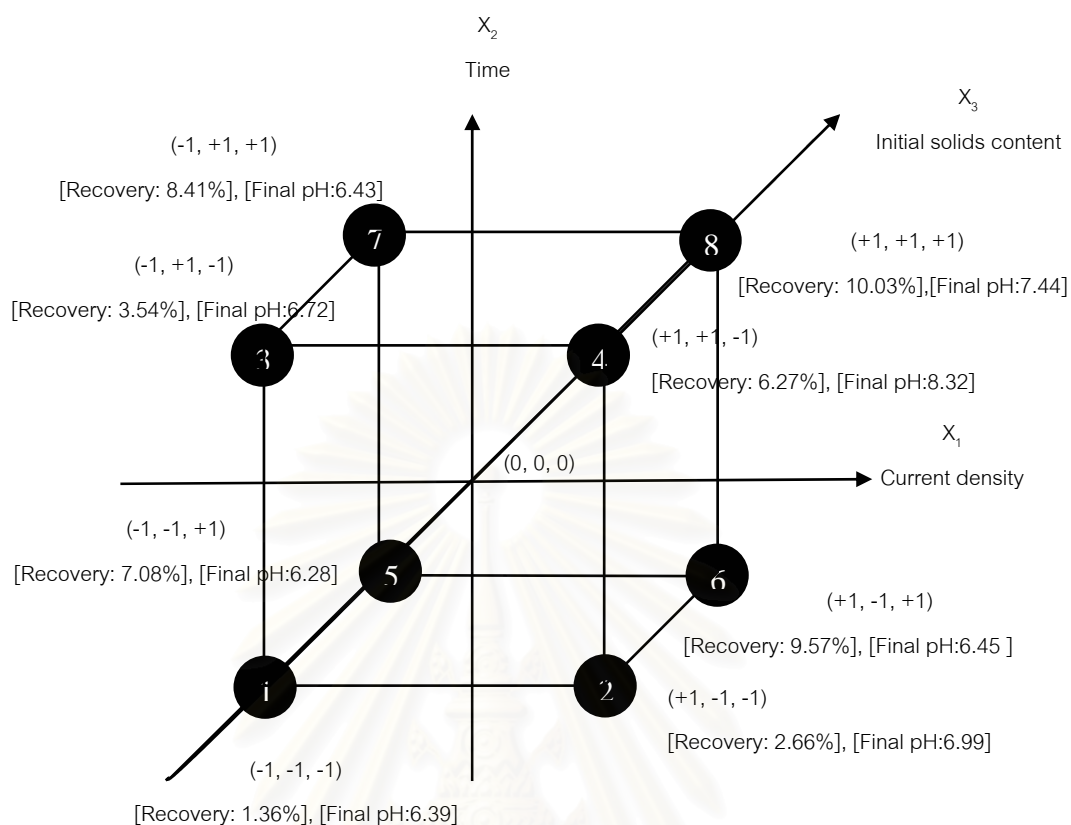
Figure 4.9 Geometric representation of the test result of iron electrodes at pH 6

Table 4.9 Test result of lignin recovery at initial pH 8 using aluminum electrodes

Experiment	Current density	Time	Initial solids content	Additional Lignin recovery by electrochemical process, Y (%)
1.	-1	-1	-1	-7.08
2.	1	-1	-1	-9.33
3.	-1	1	-1	-14.18
4.	1	1	-1	-11.88
5.	-1	-1	1	-1.16
6.	1	-1	1	-2.04
7.	-1	1	1	-0.99
8.	1	1	1	-1.11

4.3.1.1.1 Main Effect of Current Density

The average effect of current density, E_1, can be calculated by averaging the contrast between a pair of test between low and high level of current density while the other two variables are held constant. This can be written in equation as

$$E_1 = (1/4) [(Y_2-Y_1)+(Y_4-Y_3)+(Y_6-Y_5)+(Y_8-Y_7)]$$
$$= -0.24\%$$

Geometrically, the main effect of current density is the difference between the average test result on plane II (high level) of the current density and the average test result on plane I (low level of current density) as shown in Figure 4.10. It can be defined by equation as

$$E_1 = \frac{Y_2+Y_4+Y_6+Y_8}{4} - \frac{Y_1+Y_3+Y_5+Y_7}{4}$$
$$= -0.24\%$$

This main effect of current density tells us that on the average, over the ranges of the variables studied in this investigation, the effect of changing in current density from low to high level is to decrease the recovery by 0.24%.

4.3.1.1.2 Main Effect of Time

The average main effect of time, E_2, can be found by comparing the four pairs of tests to see the effect of time when the other factors were kept constant. It can be written as

$$E_2 = (1/4) [(Y_3-Y_1)+(Y_4-Y_2)+(Y_7-Y_5)+(Y_8-Y_6)]$$
$$= -2.14\%$$
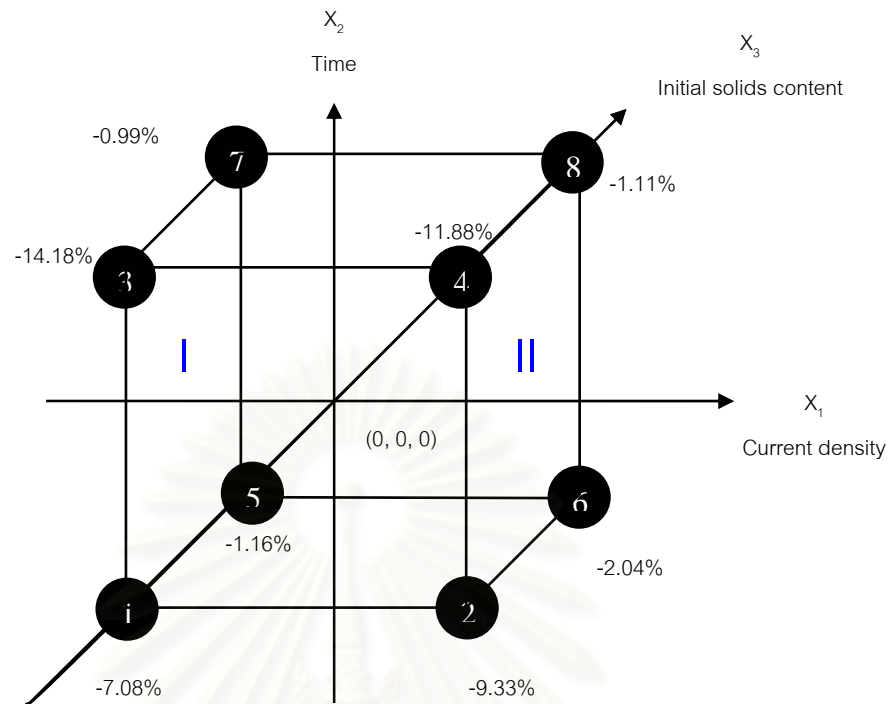
Figure 4.10 Geometric representation of the additional lignin recovery by

electrochemical process showing main effect of current density of aluminum

electrode at pH 8

Geometrically, the average effect of time is the difference

between the average result on plane IV (high level of time) and the

average result on plane III (low level of time) as shown in Figure 4.11.

The average effect of time is -2.14%, which mean that on the average, an

increase in time from low to high level decrease the lignin recovery by

2.14

4.3.1.1.3 Main Effect of Initial Solids Content

With a similar manner, the average main effect of initial solids

content, E_3, can be found by comparing the four pares of tests to see the

effect of initial solids when the other factors were kept constant. It can be

written as

$$E_3 = (1/4) [(Y_5-Y_1)+(Y_6-Y_2)+(Y_7-Y_3)+(Y_8-Y_4)]$$

$$= 9.29\%$$
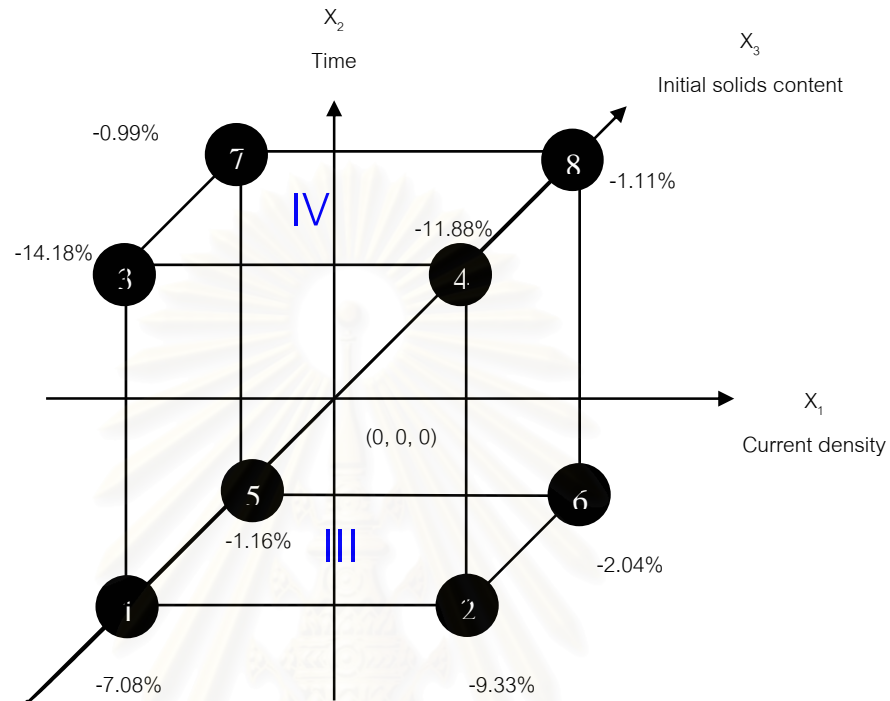
Figure 4.11 Geometric representation of the additional lignin recovery by electrochemical process showing main effect of time of aluminum electrode at pH 8

Geometrically, the average effect of time is the difference between the average result on plane VI (high level of initial solids content) and the average result on plane V (low level of initial solids content) as shown in Figure 4.12. The average effect of time is 9.29%, which mean that on the average, an increase in initial solids content from low to high level gives rise to the lignin recovery of 9.29 %, which is the highest main effect among all.
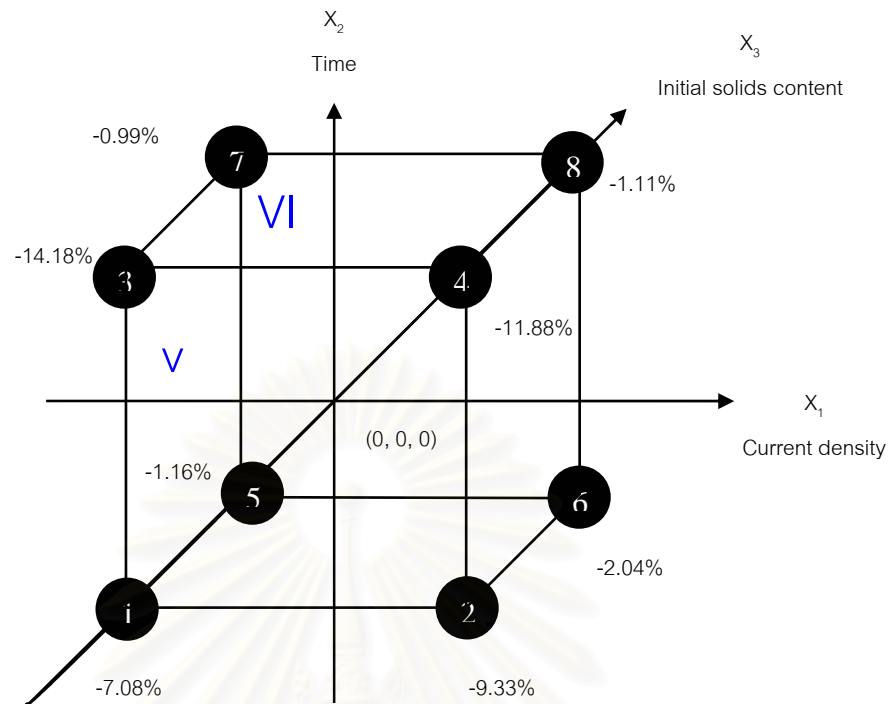
Figure 4.12 Geometric representation of the additional lignin recovery by

electrochemical process showing main effect of initial solids content of

aluminum electrode at pH 8

4.3.1.1.4 Interaction Effect of Current Density and Time

Interaction between current density and time, E_1E_2, can be found by using two-way diagram. The interaction effect between current density and time can be found by compressing the cube along the initial solids content axis. By compressing the cube, the response values for a given current density and time combination across the high and low levels of initial solids content are averaged. The geometrical representation of the 2^3 factorial that used to compress is shown in Figure 4.13 (a) and the two-way diagram showing the compressed square is in Figure 4.13 (b).

To calculate it numerically, the effect of current density is 1.09% when time is high and -1.22% when time is low. The average difference

(a)

(b)
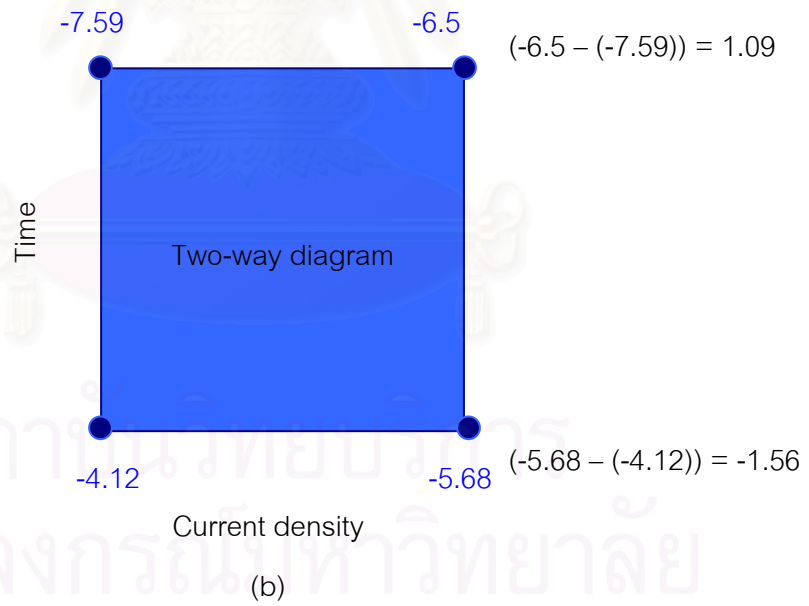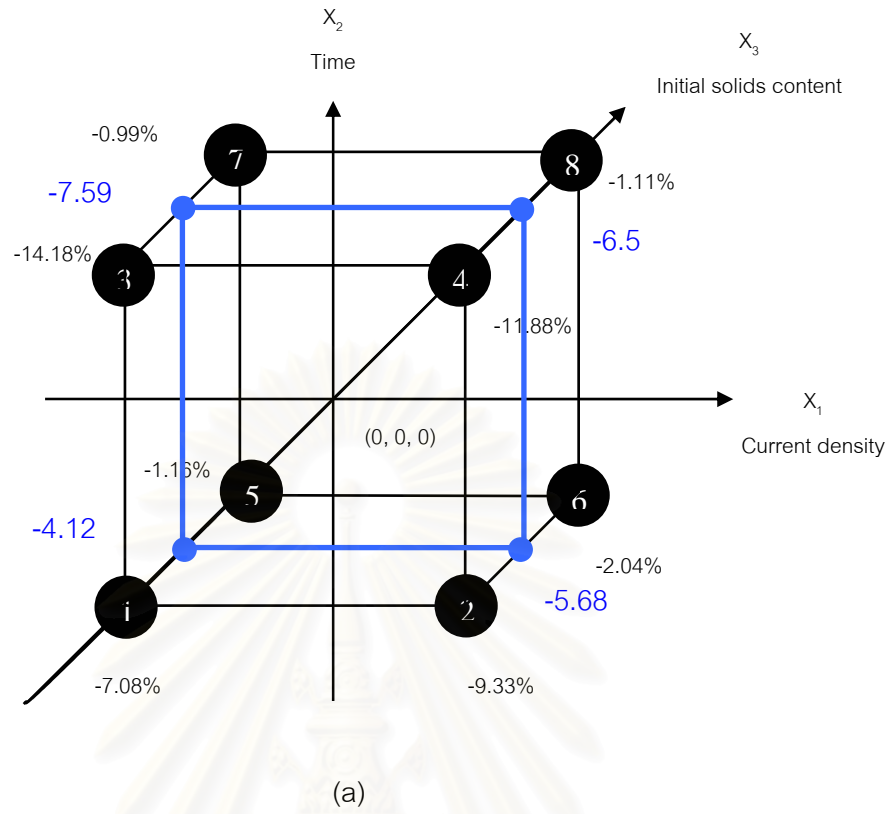
Figure 4.13 Two – factor interaction: current density and time of aluminum at pH 8

between these two effects is the interaction between current density and time. Therefore, the interaction effect of current density and time, E_{12} is

$$E_{12} = (\ 1.09 - (-1.56))/2$$
$$= 1.32 \ \%$$

4.3.1.1.5 Interaction Effect of Current Density and Initial Solids Content

Interaction between current density and initial solids content, E_1E_3, can be found by using two-way diagram in similar manner as of current density and time. The interaction effect between current density and initial solids content can be found by compressing the cube along the time axis. The geometrical representation of the 2^3 factorial that used to compress is shown in Figure 4.14 (a) and the two-way diagram showing the compressed square is in Figure 4.14 (b). To calculate it numerically, the effect of current density is -0.5% when the initial solids content is high and 0.02% when the initial solids content is low. The average different between these two effects is the interaction between current density and initial solids content. Therefore, the interaction effect of current density and initial solids content, E_{13} is

$$E_{13} = (\ -0.5 - 0.02)/2$$
$$= -0.26 \ \%$$

4.3.1.1.6 Interaction Effect of Time and Initial Solids Content

Interaction between time and initial solids content, E_2E_3, can be found by compressing the cube along the current density axis. The geometrical representation of the 2^3 factorial that used to compress is shown in Figure 4.15 (a) and the two-way diagram showing the compressed square is in Figure 4.15 (b).

To calculate it numerically, the effect of initial solids content is 11.98% when time is high and 6.6% when time is low. The average
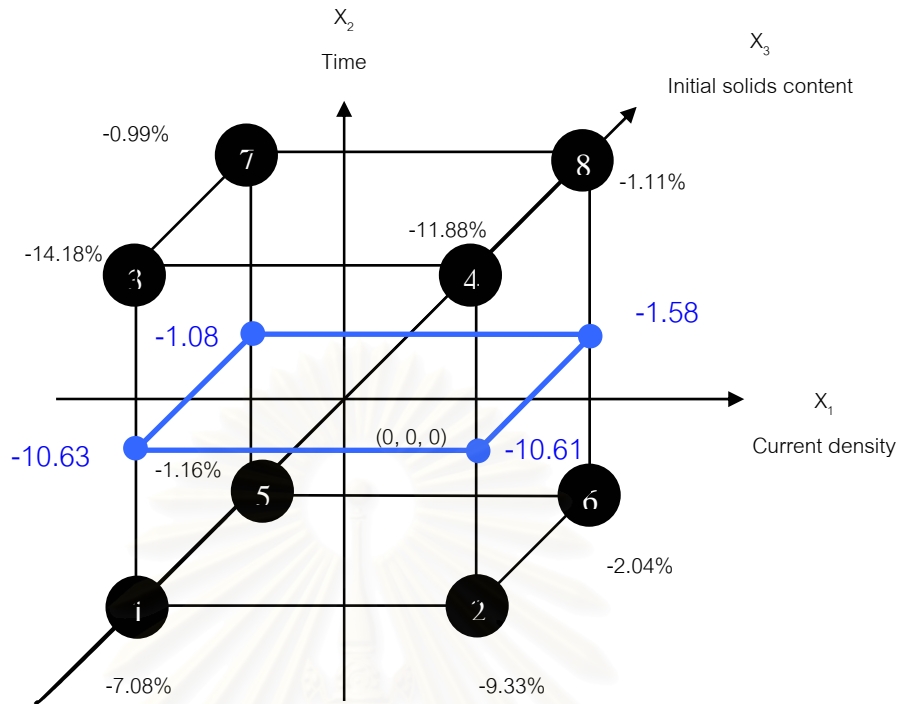
(a)
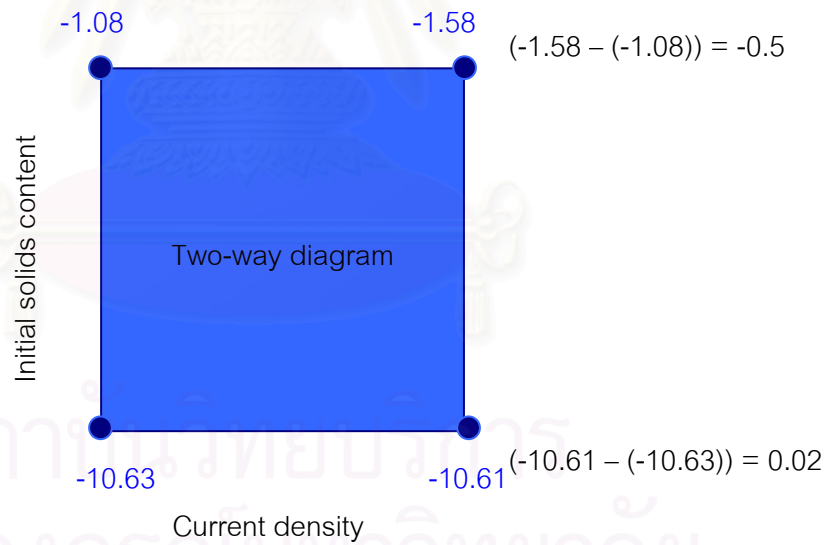
(b)

Figure 4.14 Two – factor interaction: current density and initial solids content of

aluminum electrodes at pH 8

(a)

(-1.05 – (-13.03)) = 11.98

(-1.6 – (-8.20)) = 6.6
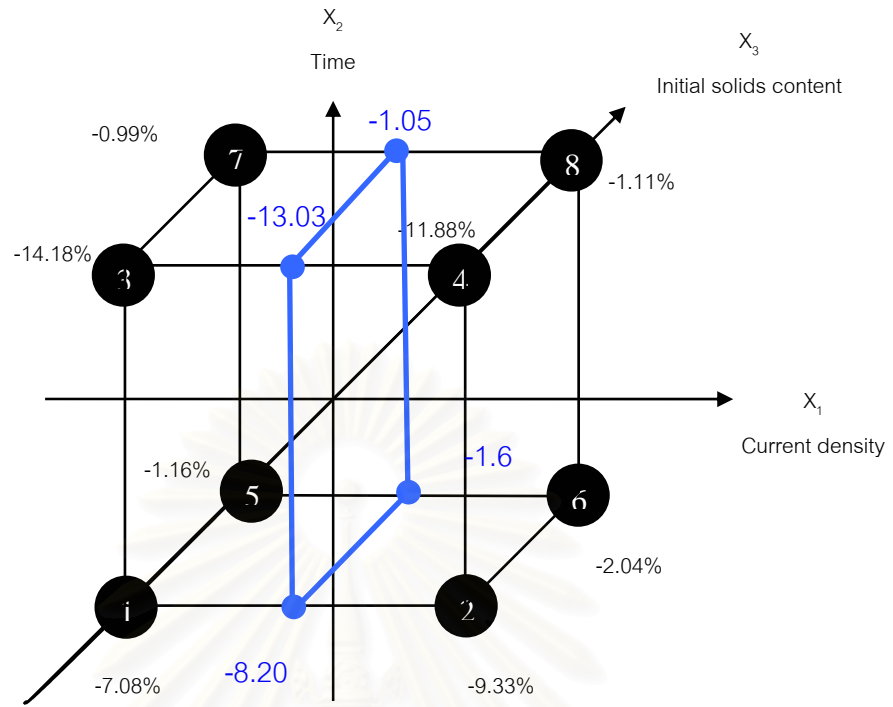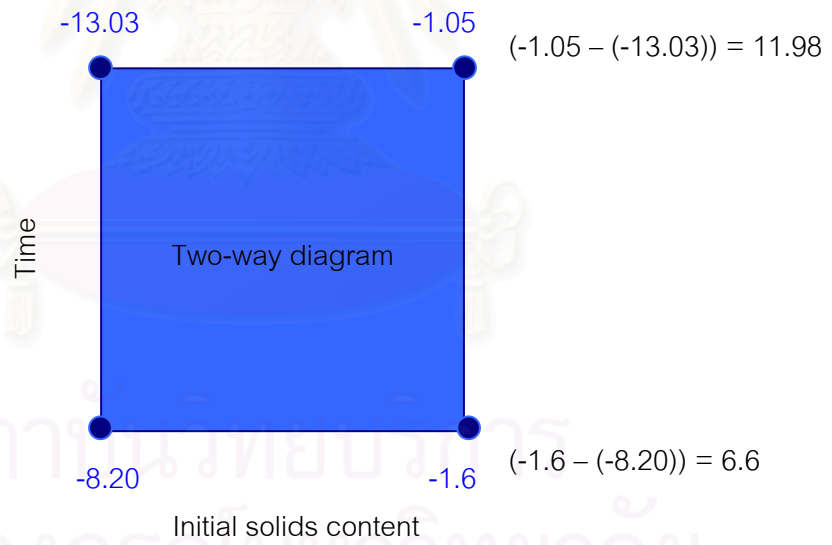
(b)

Figure 4.15 Two – factor interaction: Time and initial solids content of aluminum

electrodes at pH 8

different between these two effects is the interaction between time and initial solids content. Therefore, the interaction effect of time and initial solids content, E_{23} is

$$E_{23} = (11.98 - 6.6)/2$$
$$= 2.69 \%$$

4.3.1.1.7 The Three Factors Interaction Effect

The interaction effect of three factors, which are current density, time, and initial solids content (E_{123}) can be calculated by considered the effect of the two-factor interaction between current density and time locally, that means, cube is not compressed along the initial solids content axis. Figure 4.16 (a) shows the geometric representation of plane being considered. Figure 4.16 (b) and Figure 4.14 (c) show the two squares that are the two-way diagram that can be used to calculate two-factor interactions of current density and time E'_{12} and E''_{12} . Therefore, the estimation of the three-factor interaction can be obtained by finding the average difference in two local two-factor interaction E'_{12} and E''_{12}:

$$E_{123} = (E''_{12} - E'_{12})/2$$
$$= (0.38-2.28)/ 2$$
$$= -0.95 \%$$

Summary of the Effects

The main effects and interaction effects of lignin recovery using aluminum electrode at pH 8 can be summarized as shown in Table 4.10. It can be seen that among the average main effect, initial solids content has the most positive effect on lignin recovery where increase from low to high level of initial solids content will increase the recovery averagely for 9.29%. Time and current density have lower effect on lignin recovery consecutively and also in negative direction. For the interaction effects, time and initial solids content has the most effect then current density and time, where

(a)
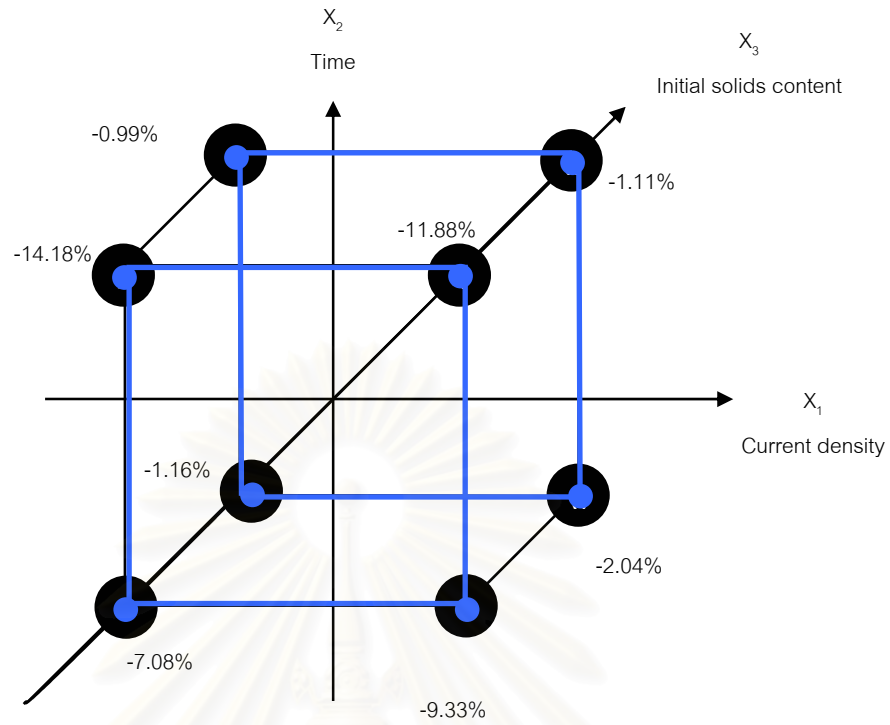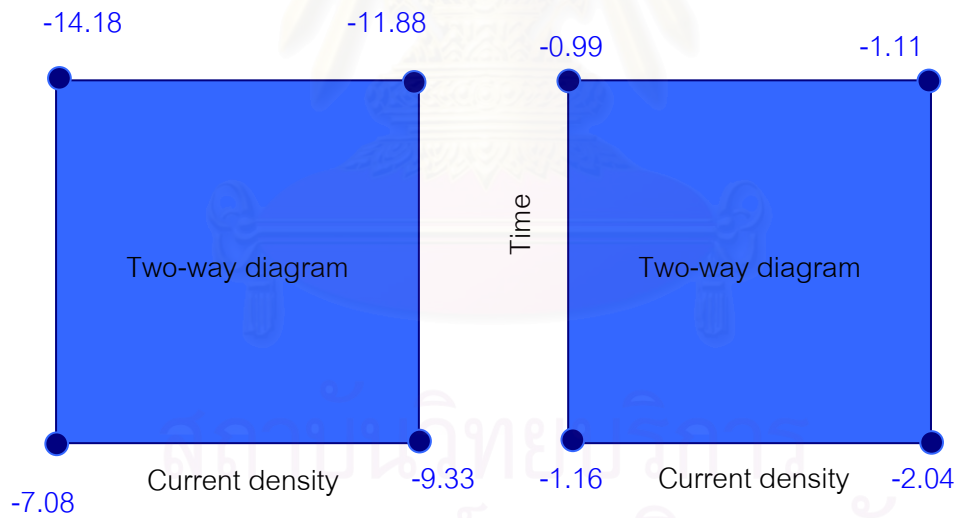
(b)   (c)

Figure 4.16 Three – factor interaction of aluminum electrodes at pH 8

increase each factor from low to high level will increase the recovery for 2.69% and 1.3% consecutively. However, the interaction effect between current density and initial solids content and interaction effect of all factors give negative result to the recovery.

Since the recovery of lignin using aluminum electrodes at pH 8 was not accomplished. The resuspension had occurred, therefore, the model was not constructed, only analysis of main and interaction effects were done.

Table 4.10 Summary of main effects and interaction effects of lignin recovery using
aluminum electrodes at pH 8

	Main	Effect			Interaction Effect		
Current density, E_1	Time, E_2	Initial solids content, E_3		E_{12}	E_{13}	E_{23}	E_{123}
-0.24	-2.14	9.29		1.3	-0.26	2.69	-0.95

4.3.1.2 Initial pH of 7

Other than the analysis method used in pH 8, the generalized method for effects calculation can be done. The simplified calculation procedure can be done by multiply the result with the coded values of each column of factor as shown in calculation matrix for 2^3 factorial design in Table 4.11.

Table 4.11 Calculation matrix for 2^3 factorial design for aluminum electrodes at pH 7

Test	Main effects				Interaction effects				Y, %
	I	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	
1	+	-1	-1	-1	+1	+1	+1	-1	-4.76
2	+	+1	-1	-1	-1	-1	+1	+1	-4.31
3	+	-1	+1	-1	-1	+	-1	+1	-1.78
4	+	+1	+1	-1	+1	-1	-1	-1	-11.52
5	+	-1	-1	+1	+1	-1	-1	+1	0.44
6	+	+1	-1	+1	-1	+	-1	-1	1.26
7	+	-1	+1	+1	-1	-1	+1	-1	-0.01
8	+	+1	+1	+1	+1	+1	+1	+	-1.23

Therefore, the average for the main effect of current density (E_1), time (E_2) and initial solids content (E_3) can be calculated as followed.

x_1		Y	x_2		Y	x_3		Y
-1	X	-4.76	-1	X	-4.76	-1	X	-4.76
+1	X	-4.31	-1	X	-4.31	-1	X	-4.31
-1	X	-1.78	+1	X	-1.78	-1	X	-1.78
+1	X	-11.52	+1	X	-11.52	-1	X	-11.52
-1	X	0.44	-1	X	0.44	+1	X	0.44
+1	X	1.26	-1	X	1.26	+1	X	1.26
-1	X	-0.01	+1	X	-0.01	+1	X	-0.01
+1	X	-1.23	+1	X	-1.23	+1	X	-1.23
Sum	=	-9.68	Sum	=	-7.16	Sum	=	22.84
Sum/4	=	-9.68/4	Sum/4	=	-7.16/4	Sum/4	=	22.84/4
E_1	=	-2.42	E_2	=	-1.79	E_3	=	5.71

The interaction effects of current density and time (x_{12}), current density and initial solids content (x_{13}), time and initial solids content (x_{23}), and three factors interaction effect (x_{123}) can be calculate in similar manner as show below.

x_1x_2		Y	x_1x_3		Y
+1	X	-4.76	+1	X	-4.76
-1	X	-4.31	-1	X	-4.31
-1	X	-1.78	+	X	-1.78
+1	X	-11.52	-1	X	-11.52
+1	X	0.44	-1	X	0.44
-1	X	1.26	+	X	1.26
-1	X	-0.01	-1	X	-0.01
+1	X	-1.23	+1	X	-1.23
Sum	=	-12.24	Sum	=	8.88
Sum/4	=	-12.24/4	Sum/4	=	8.88/4
E_{12}	=	-3.06	E_{13}	=	2.22

x_2x_3		Y	$x_1x_2x_3$		Y
+1	X	-4.76	-1	X	-4.76
+1	X	-4.31	+1	X	-4.31
-1	X	-1.78	+1	X	-1.78
-1	X	-11.52	-1	X	-11.52
-1	X	0.44	+1	X	0.44
-1	X	1.26	-1	X	1.26
+1	X	-0.01	-1	X	-0.01
+1	X	-1.23	+1	X	-1.23
Sum	=	-1.28	Sum	=	8.16
Sum/4	=	-1.28/4	Sum/4	=	8.16/4
E_{23}	=	-0.32	E_{123}	=	2.04

From the calculations above, the effects can be summarized in Table 4.12.

Table 4.12 Summary of main effects and interaction effects of lignin recovery using aluminum electrodes at pH 7

Main	Effect			Interaction Effect			
E_1	E_2	E_3		E_{12}	E_{13}	E_{23}	E_{123}
-2.42	-1.79	5.71		-3.06	-2.22	0.32	2.04

From the result, it can be seen that initial solids content has the major positive effect on lignin recovery where increase from low to high level of initial solids content will increase the recovery by 5.71%. However, the other two main effect have lower in magnitude and opposite direction result on lignin recovery. For interaction effects, effect of current density and time has the most effect on lignin recovery however, in negative direction and also current density with initial solids content. However, the effect of the three-factor has the positive direction

as same as effect of time and initial solids content, but it has smaller magnitude on the recovery.

In this pH of study, the recovery was not accomplished properly, therefore, the model was not constructed. Only the average main effects and interaction effects were analyzed.

4.3.1.3 Initial pH of 6

The average main effects and average interaction effect of lignin recovery using aluminum electrodes at pH 6 can be calculated by the same manner as in pH 7. The summary of all calculated effects are summarized in Table 4.13.

Table 4.13 Summary of main effects and interaction effects of lignin recovery using aluminum electrodes at pH 6

Main	Effects			Interaction Effects			
E_1	E_2	E_3		E_{12}	E_{13}	E_{23}	E_{123}
3.72	0.3	6.58		-2.24	2.01	-1.05	0.93

From the result, it can be seen that all of the effects have difference calculated value. It tells us that not all of them have the same effect on lignin recovery, however, some might have closed values. The initial solids content has the highest impact on lignin recovery where 6.58% lignin recovery will rise after increasing from low to high level. This result is agreed by the results from pH 8 and pH 7. Current density has second most impact on increasing lignin recovery from low to high level of 3.72%. Effect of time is found to be 0.3%, however, this value is considered very low and could possibly be the reflection of experimental error, since this effect calculation is the average of the difference between pairs of test where the real effect should be 0 (Devor, 1992). Therefore, the effect of time can be neglected and said to be 0. For the interaction effect, effect of current density with time and time with initial solids content have negative impact on the recovery, while the effect of current density with initial solid content and the three factors interaction have the positive impact to lignin recovery.

From the test results on lignin recovery, model can be constructed to predict the precipitation through the equation below

$$\hat{Y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \qquad (4.9)$$

Where b_0 = average of the summation of all the resultant Y

b_n = $E_n/2$

x_n = coded value

Therefore, the model can be written as

$$\hat{Y} = 7.71 + 1.86 x_1 + 3.29 x_3 - 1.12x_1x_2 + 1.00x_1x_3 + -0.52x_2x_3 + 0.46x_1x_2x_3 \qquad (4.10)$$

From this model, the coefficient of variation or R^2 value was calculated to be 0.99. The real recovery values and the calculated values from the models of these eight conditions are shown in Table 4.14. This is a very high value of R^2, which mean that the model can be used to predict almost exactly the of lignin recovery. However, this is the result of very high value of B_0, 7.71, when compare to other B values. This reflexes that

Table 4.14 Real experimental values and calculated values of lignin recovery using aluminum electrodes at pH 6

Experiment	Current	Time	Initial solids content	Recovery from real experiments, %	Calculated recovery values from model, %
1	-1	-1	-1	1.30	1.46
2	1	-1	-1	6.18	6.34
3	-1	1	-1	5.81	5.66
4	1	1	-1	4.37	4.22
5	-1	-1	1	7.85	8.00
6	1	-1	1	14.89	15.04
7	-1	1	1	8.41	8.28
8	1	1	1	12.83	12.68

the model have not include other important factor or factors, which should have major impact on lignin recovery. This factor could possibly be the pH, since pH will determined what form of metal ion will formed in the solution, thus, mainly reflex the recovery of lignin.

4.3.2 Iron Electrodes

4.3.2.1 Initial pH of 8

The average main effects of current density (E_1), time (E_2), and initial solids content (E_3) and average interaction effects of current density and time (E_{12}), current density and initial solids content (E_{13}), time and initial solids content (E_{23}), and the three-factors effect (E_{123}) of lignin recovery using iron electrodes at pH 8 were calculated. The summary of all calculated effects are summarized in Table 4.15.

Table 4.15 Summary of main effects and interaction effects of lignin recovery using
iron electrodes at pH 8

Main Effects				Interaction Effects			
E_1	E_2	E_3		E_{12}	E_{13}	E_{23}	E_{123}
2.57	-5.03	3.24		2.00	0.24	1.48	-1.13

From the result, only time and the three factor effects are having negative impact on the recovery. Initial solids content, like previous results, is the factor that give highest rise to lignin recovery, 3.24%, followed by current density, 2.57%, the effect current density and time,2%, the effect of time and initial solids content,1.48%, and current density and initial solids content, 0.24%. However, due to the negative lignin recovery, the construction of model was not further developed.

4.3.2.2 Initial pH of 7

The average main effects of current density (E_1), time (E_2), and initial solids content (E_3) and average interaction effect of current density and time

(E_{12}), current density and initial solids content (E_{13}), time and initial solids content (E_{23}), and the three-factors effect (E_{123}) of lignin recovery using iron electrodes at pH 7 were calculated. The summary of all calculated effects are summarized in Table 4.16.

Table 4.16 Summary of main effects and interaction effects of lignin recovery using iron electrodes at pH 7

Main	Effects			Interaction Effects			
E_1	E_2	E_3		E_{12}	E_{13}	E_{23}	E_{123}
1.58	0.69	6.45		0.16	2.66	-0.45	0.55

From the result, it can be seen that initial solids content has the highest effect on lignin recovery among all effects where increase initial solids from low to high level will result in increasing of lignin recovery by 6.45%. Follow with effect of current density and initial solids content where increase of both factors from low to high level will give rise to lignin recovery of 2.66%. Then, effect of current density alone where increasing of low to high level of current density will increase the recovery 1.58%. Then follow with time,0.69%, the three factor effect,0.55%, and effect of current density and time,0.16%, while effect of time and initial solids content will give negative result of 0.45% to the recovery.

Due to some resuspension and some negative results of lignin recovery, the model was not further developed.

4.3.2.3 Initial pH of 6

The average main effects of current density (E_1), time (E_2), and initial solids content (E_3) and average interaction effect of current density and time (E_{12}), current density and initial solids content (E_{13}), time and initial solids content (E_{23}), and the three-factors effect (E_{123}) of lignin recovery using iron electrodes at pH 6 were calculated. The summary of all calculated effects are summarized in Table 4.17.

Table 4.17 Summary of main effects and interaction effects of lignin recovery using iron electrodes at pH 6

Main Effects				Interaction Effects			
E_1	E_2	E_3		E_{12}	E_{13}	E_{23}	E_{123}
2.03	1.90	5.31		-0.14	0.02	-0.1	-0.57

From the result, it can be seen that among the factors, initial solids content will has the most positive effect on lignin recovery where in this case, increase from low to high level of current density will increase lignin recovery by 5.31%. Follow by current density as the second most effective with recovery, increased by 2.03 when factor is increased from low to high level, and time is the third with increasing of 1.9% lignin recovery when increase from low to high level of current density. For interaction effects, the values are quite small. The effect of current density and time, and current density and initial solids content can be neglect, since it is very small and could possibly be the reflection of the experimental error. And the rest are having negative impact on the recovery. The model can be written as

$$\hat{Y} = 6.12 + 1.02x_1 + 0.95x_2 + 2.66x_3 + 0.07x_1x_2 + -0.28x_1x_2x_3 \qquad (4.11)$$

Where b_0 = average of the summation of all the resultant Y

$b_n = E_n/2$

x_n = coded value

From this model, the coefficient of variation of R^2 value was calculated to be 0.97. The calculated and experimental values are compared in the Table 4.18. This is also a very high value for coefficient of variation. The model must be very accurate in predicting the result. However, we can also see that the B_0 value is very high compare to other B values, which should be the values that have more effect on the recovery. This implied that there are still some other variable that has more effect on lignin recovery that have not been included in the study. One of those possible factors is pH.

Table 4.18 Real experimental values and calculated values of lignin recovery using iron electrodes at pH 6

Experiment	Current	Time	Initial solids content	Recovery from real experiments, %	Calculated recovery values from model, %
1	-1	-1	-1	1.36	1.84
2	1	-1	-1	2.66	3.18
3	-1	1	-1	3.54	3.04
4	1	1	-1	6.27	5.78
5	-1	-1	1	7.08	6.6
6	1	-1	1	9.57	9.06
7	-1	1	1	8.41	8.92
8	1	1	1	10.03	10.54

4.4 Model Validation

From the models developed using design of experiment, they can be validated by compare the result of lignin recovery tests of other conditions but still within the ranges of the factors study. Three conditions of lignin recovery were done and used in model validation.

4.4.1 Aluminum Electrode at pH 6

The tested conditions of aluminum electrodes at pH 6 and the result of the tests are shown in Table 4.19 and Table 4.20.

Table 4.19 Test conditions of aluminum electrode at pH 6

Test	Current density, mA/cm^2	Time, min	Initial solids content, %
1	6.8	5	15.3
2	4	7	15.3
3	4	5	14

Table 4.20 Result of test condition of aluminum electrode at pH 6

Test	Current density	Time	Initial solids content	Additional recovery by electrochemical process, %	Lignin recovery from model, %	Error of model*, %
1.	0.4	-1	1	2.88	12.9	347.92
2.	-1	-0.6	1	5.57	8.056	44.63
3.	-1	-1	0.51	5.5	6.39	16.18

* Error of model = [(│Value from experiment – Value from model│/ Value of experiment)] x 100

From the result, it can be seen that the error of the model is ranging from 16.18% to 347.92%. The highest error occurred with the variation of current density, which is the first test. This is possible, since current density will be affected by pH of the solution, thus, affecting form of ions that would be created. This impacted mainly on lignin recovery. For second test, error is 44.63%, which is quite high. This is possibly due to the experimental error together with the fact that time of the reaction will also affect pH of solution as well. Therefore, cause of error in this condition is similar to that of the first test. The last one, initial solids content was varied. The error of the model is 16.18%, which is should be an acceptable error, since it does not exceed 20% This error indicates that factor of initial solids does not depend or affect other factors. When compare the results from the tests to those in the prior experiments, test 1 to experiment 5 and 6, test 2 to experiment 5 and 7, and test 3 with experiment 1 and 5, it can be seen that only test three's result has the result lined in between the previous experiments. Test one and two's results have results that were not following the trend in the previous experiments. However, the error of all tests may also be as a result of experimental error, error of the model, and perhaps might be the result of the foam created that could interfered the recovery.

4.4.2 Iron Electrode at pH 6

The tested conditions of aluminum electrode at pH 6 and the result of the tests are shown in Table 4.21 and Table 4.22.

Table 4.21 Test conditions of iron electrode at pH 6

Test	Current density, mA/cm2	Time, min	Initial solids content, %
1	8	5	15.3
2	2	7	15.3
3	2	5	14

Table 4.22 Result of test conditions of iron electrode at pH 6

Test	Current	Time	Initial solids content	Additional recovery by electrochemical process, %	Lignin recovery from model, %	Error of model, %
1.	0.2	-1	1	0.04	8.06	200.5
2.	-1	-0.6	1	8.49	7.11	16.25
3.	-1	-1	0.51	6.84	5.47	20.00

From the result, it can be seen again that the error of the model from the first test is very high, 200.5%, which is surly not acceptable. This error should due, mainly, to the same reason as of aluminum electrode where pH of solution was affected by current density, thus, resulted in error of amount of lignin recovery. For second test, error is 16.25%, which is possibly as a result of pH change due to change in reaction time. The last test reflexes the accuracy of the model when initial solids content is varied. The error is 20% and it should be as a result of experimental error and error of the model itself, which surely will have some contribution to all the results of test conditions. If compare the results from the tests to those in prior experiments, test 1 to experiment 5 and 6, test 2 to experiment 5 and 7, and test 3 with experiment 1 and 5, it can be seen that only test three's result has the result lined in between the previous experiments. Test one and two's results have results that were not following the trend in the previous experiments. These results are agreed between aluminum and iron electrodes. However, the error of all tests may also be as a result of experimental error, error of the model, and perhaps might be the result of the foam created that could interfered the recovery.

4.5 Economics Analysis

Other than main effects and interaction effects of factors and the performance of the model, the economics aspect of the processes should be put into considered as well. The basic economics analysis between aluminum and iron process can be done by compare their performance and cost of input among them. Table 4.23 shows the economics comparison values of aluminum and iron electrodes. For aluminum, the optimum condition occur at high current density, low time, and high initial solids content, which are 8 mA/cm^2, 5 min., and 15.3% initial solids content with the performance of 14.89% lignin removal by electrochemical process. This will equal to 0.67 A*min/% removal by electrochemical process. For iron electrodes, the optimum condition is at high current density, time, and initial solids content with removal by electrochemical process of 10.03%. This can be converted to 4.49 A*min/%removal of electrochemical process. From this comparison values, aluminum electrodes is 6.68 times better than iron electrodes. If includes the prices of the electrodes into consideration, aluminum electrodes will be about 1.2 times more efficient than the iron electrode, since price of aluminum is about 200 baht/kg and iron is about 36 baht/kg.

Table 4.23 Economics comparison of aluminum and iron electrodes

Electrode	Current density, mA/ cm^2	Surface area, cm^2	Time, min.	Removal by electrochemical process, %	Comparison Unit, A*min/ % removal
Aluminum	8	25	5	14.89	0.67
Iron	12	25	15	10.03	4.49

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

1. Lignin recovery using acidification together with electrochemical process using aluminum and iron electrodes were found to be optimum and pH 6, where all the lignin recoveries were achieved. The highest recovery of lignin using aluminum electrodes was 82.86% where 14.89% was the result of electrochemical process, which occurred at high current density, low contact time, and high initial solids content. The highest recovery of lignin using iron electrodes reached maximum of 78% where 10.03% was as the result of electrochemical process at high current density, time, and initial solids content. These conditions were considered to be the optimum conditions for lignin recovery for aluminum and iron electrodes yielded from this 2^3 factorial design experiments. However, at pH 8 and 7, lignin recoveries were not accomplished for both electrodes. This was due to the different metal ions formed in these pH ranges, which did not support the precipitation of lignin. The recovery of optimal conditions might considered low for industries to invest in this technology, however, this finding still have a lot of rooms for improvement. This is only the beginning of the new discovery. The study of effect of pH, temperature, full coagulation and flocculation process, and etc can be included in further study to improve the efficiency of lignin recovery using electrochemical process before it is scaled up to the real performance.

2. From the study, it was found that factors studied, current density, time, and initial solids content, had different contribution to lignin recovery. It was found that initial solids content had the most positive effect on lignin recovery for both aluminum and iron electrodes. Second was current density and third was time. However, their magnitudes are difference according to pH and type of electrode. For interaction effects, the order of significant, magnitude, and direction were different among electrode material and pH.

3. The models for lignin recovery at pH 6 using aluminum and iron electrodes were constructed using design of experiment or 2^3 factorial design. However, it had to be noted that these models were particularly designed for eucalyptus based black liquor, which underwent soda pulping process. From the models, it was found that the R^2 values of both equations were much closed to 1, 0.99 for aluminum electrodes and 0.97 for iron electrodes. However, the B_0 values of the equations indicated that there were perhaps other factor or factors, which have major impact on lignin recovery that this model have not included. The results of models validation also confirmed the idea. Therefore, the models were not used for further study of optimal conditions, which could be calculated using model but rather specified from the eight condition experiments. The possible factor that should have major impact on lignin recovery is pH because pH plays a major role in forming ions and the form of ions formed will determine the precipitation reaction of the system.

4. When comparing lignin recovery by electrochemical process after pH adjustment to 6 to acidification alone, there are several advantages associated with electrochemical process. First, with electrochemical process, less caustic chemical for lowering pH will be used to yield the same amount of lignin recovery. Second, the remaining wastewater will have a pH range within the discharging standard (pH 6-8), therefore, no pH adjustment is needed after the recovery process. Third, there will be sulfur gas created during acidification process due to sulfur contained in the black liquor itself and the acid used for acidification. However, with the electrochemical process, there is no corrosive gas created but foam, which is the result of hydrogen gas production that might disturb the process if it exceeded the container or in contact with the circuit.

5. In the economics point of view, aluminum electrode will have about 6 times higher efficiency than iron electrodes where the comparison units for aluminum electrodes is 0.67 A*min / %recovery and 4.49 A*min / %recovery for iron electrodes. When include price of electrodes metal into consideration, aluminum still have higher efficiency of about 1.2 times higher than iron, since price of aluminum is 200 baht/kg. and iron is 36 baht/kg.

5.2 Recommendation

The ability of the models constructed in this study is limited due to unincluded factor that should have major effect on lignin recovery. The factors of pH, which may have confounding effect with current density and time, together with current density and time should be studied further in order to develop more successful model. Also, temperature and full coagulation and flocculation process are another factors that should put into consideration since it also affect amount of lignin recovered.

Further study on the chemical structure and quality of recovered lignin can be further investigated and compared with other recovery process lignin, for example acidification and membrane filtration.
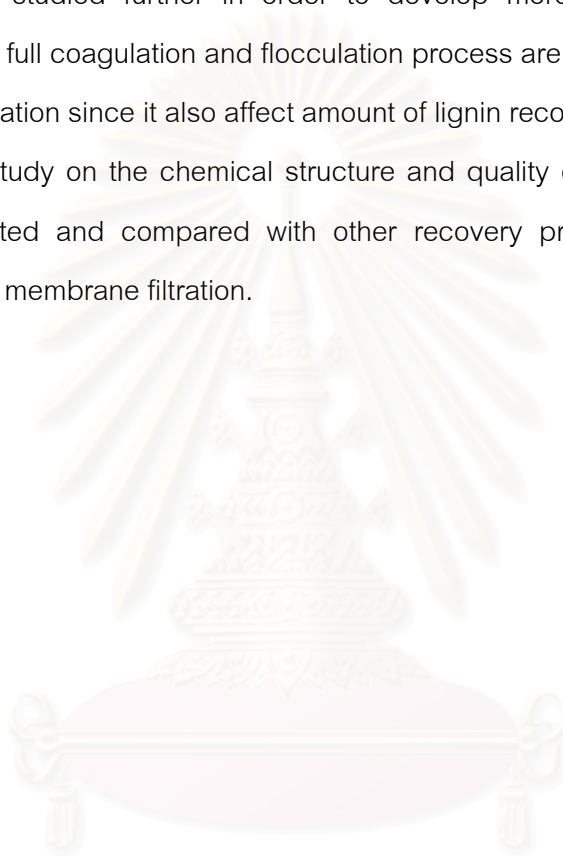
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APPENDICES

APPENDIX A

LIGNIN CALIBRATION CURVE

Lignin Calibration Curve

Lignin calibration curve was made by dilutions of standard lignin powder at different concentrations. Absorbance of lignin solutions were measured using UV-spectrophotometer at wavelength of 280 nm.

Table A-1 Lignin absorbance at different concentrations

Lignin concentration in solution, g/L	Absorbance at 280 nm
6.00E-03	0.093
9.00E-03	0.158
3.00E-02	0.491
6.00E-02	0.939
9.00E-02	1.498
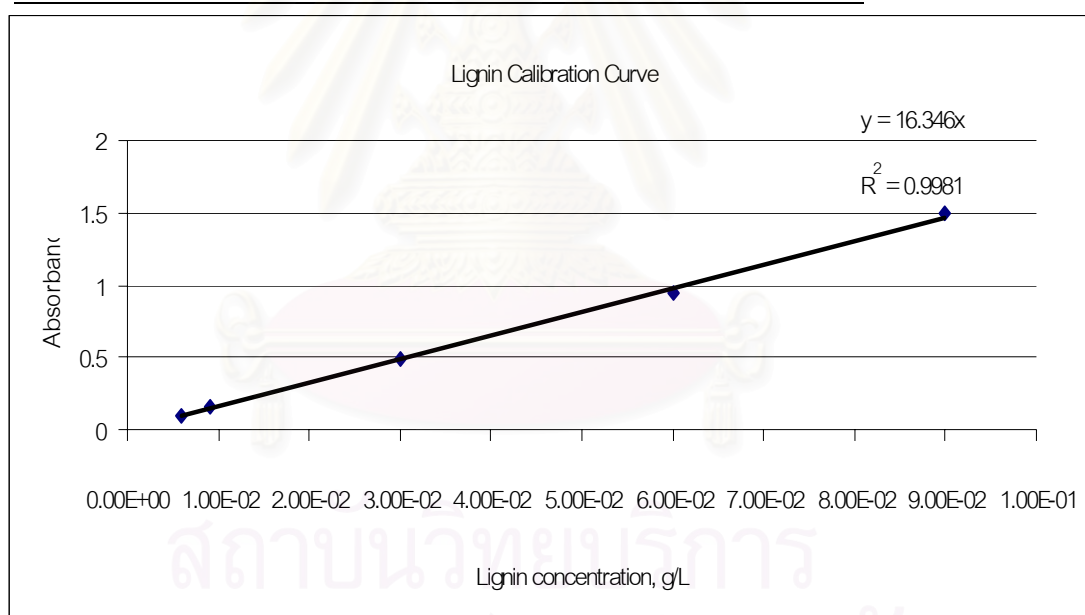
Figure A-1 Lignin calibration curve

APPENDIX B

BACKGROUND MEASUREMENT BEFORE ELCTROCHEMICAL PROCESS

Table B-1: Black liquor condition measurement (before electrochemical process)

Black Liquor Conditions		UV adsorption	Dilution, time	Lignin concentration, g/L	Avg. lignin concentration, g/L	Lignin recovery, %	CV, %
pH	% solids						
12.5 (original condition)	15.3 (original condition)	0.533	2500	81.84			
		0.530	2500	81.38			
		0.536	2500	82.30	81.84	-	
	10	0.120	5000	37.84			
		0.102	5000	32.36			
		0.119	5000	37.54	35.91	-	
8	15.3	0.475	1000	29.20			
		0.498	1000	30.60			
		0.508	1000	31.21	30.34	30.34	
	10	0.412	1000	25.36			
		0.409	1000	25.18			
		0.415	1000	25.55	25.36	25.36	

Table B-1: Black liquor condition measurement (before electrochemical process) (con.)

Black Liquor Conditions		UV adsorption	Dilution, time	Lignin concentration, g/L	Avg. lignin concentration, g/L	Lignin recovery, %	CV, %
pH	% solids						
7	15.3	0.471	1000	28.96			
		0.472	1000	29.02			
		0.470	1000	28.90	28.96	28.96	
	10	0.329	1000	20.30			
		0.339	1000	20.91			
		0.335	1000	20.67	20.63	20.63	
6	15.3	0.426	1000	26.22			
		0.444	1000	27.31			
		0.408	1000	25.12	26.22	53.00	
	10	0.312	1000	19.27			
		0.311	1000	19.21			
		0.314	1000	19.39	19.29	46.29	

APPENDIX C

PRELIMINARY TEST RESULT

Table C-1 Preliminary test result of aluminum electrodes at pH 7

Experiment	Current density, mA/cm^2	Time, min.	UV absorption at 280 nm.	Dilution	Lignin recovery, %	Additional lignin by electrochemical process, %
1	0.02	5	0.474	1000	64.34	-0.27
2	0.02	15	0.485	1000	63.75	-0.87
3	0.04	5	0.433	1000	67.63	3.02
4	0.04	15	0.505	1000	63.89	-0.72
5	0.04	30	0.507	1000	62.10	-2.52
6	0.08	5	0.477	1000	65.09	0.47
7	0.08	15	0.474	1000	64.57	-0.05
8	0.08	30	0.525	1000	60.76	-3.86
9	0.12	5	0.457	1000	65.84	1.22
10	0.12	15	0.506	1000	62.18	-2.44
11	0.12	30	0.532	1000	60.23	-4.38

Table C-2 Preliminary test result of iron electrodes at pH 7

Experiment	Current density, mA/cm^2	Time, min.	UV absorption at 280 nm.	Dilution	Lignin recovery, %	Additional lignin recovery by electrochemical process, %
1	0.02	5	0.467	1000	64.91	0.30
2	0.02	15	0.476	1000	64.24	-0.37
3	0.04	5	0.448	1000	66.33	1.71
4	0.04	15	0.45	1000	66.18	1.56
5	0.04	30	0.435	1000	67.30	2.68
6	0.08	5	0.436	1000	67.22	2.61
7	0.08	15	0.427	1000	67.89	3.28
8	0.08	30	0.445	1000	66.55	1.94
9	0.12	5	0.429	1000	67.74	3.13
10	0.12	15	0.465	1000	65.06	0.45
11	0.12	30	0.452	1000	66.03	1.41

APPENDIX D

EXPERIMENTAL RESULTS

Table D -1 Lignin recovery results of aluminum electrodes at pH 8

Experi ment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery , %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process, %	Final pH
1	-1	-1	-1	0.457		1000	22.15		-7.23		
				0.447		1000	23.94		-5.44		
				0.465	2.03	1000	20.79	22.29	-8.59	-7.08	8.17
2	1	-1	-1	0.472		1000	19.60		-9.78		
				0.464		1000	21.04		-8.33		
				0.473	1.08	1000	19.51	20.05	-9.87	-9.33	8.20
3	-1	1	-1	0.493		1000	16.10		-13.27		
				0.491		1000	16.36		-13.02		
				0.510	2.12	1000	13.12	15.20	-16.26	-14.18	8.31
4	1	1	-1	0.481		1000	18.06		-11.32		
				0.487		1000	17.04		-12.34		
				0.485	0.63	1000	17.38	17.49	-12.00	-11.88	8.53

Table D -1 Lignin recovery results of aluminum electrodes at pH 8 (con.)

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.503		1000	62.44		-0.49		
				0.525		1000	60.76		-2.17		
				0.507	2.33	1000	62.10	61.76	-0.83	-1.16	8.12
6	1	-1	1	0.534		1000	60.08		-2.85		
				0.529		1000	60.49		-2.44		
				0.507	2.73	1000	62.10	60.89	-0.83	-2.04	8.15
7	-1	1	1	0.518		1000	61.28		-1.65		
				0.526		1000	60.72		-2.21		
				0.484	4.34	1000	63.82	61.94	0.89	-0.99	8.30
8	1	1	1	0.485		1000	63.78		0.85		
				0.537		1000	59.90		-3.03		
				0.512	5.09	1000	61.76	61.81	-1.16	-1.11	8.39

Table D -2 Lignin recovery results of aluminum electrodes at pH 7

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
1	-1	-1	-1	0.356		1000	39.44		-3.12		
				0.381		1000	35.10		-7.46		
				0.359	3.79	1000	38.85	37.79	-3.71	-4.76	7.31
2	1	-1	-1	0.359		1000	38.85		-3.71		
				0.380		1000	35.27		-7.29		
				0.349	4.42	1000	40.63	38.25	-1.92	-4.31	7.48
3	-1	1	-1	0.353		1000	39.87		-2.69		
				0.353		1000	39.87		-2.69		
				0.337	2.66	1000	42.59	40.78	0.04	-1.78	7.67
4	1	1	-1	0.393		1000	33.14		-9.42		
				0.415		1000	29.39		-13.17		
				0.408	2.78	1000	30.58	31.04	-11.97	-11.52	7.73

Table D -2 Lignin recovery results of aluminum electrodes at pH 7 (con.)

Experi ment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery , %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.456		1000	65.91		1.30		
				0.473		1000	64.64		0.03		
				0.474	2.13	1000	64.61	65.05	-0.01	0.44	7.25
6	1	-1	1	0.471		1000	64.83		0.21		
				0.413		1000	69.13		4.51		
				0.486	8.43	1000	63.67	65.88	-0.95	1.26	7.41
7	-1	1	1	0.485		1000	63.75		-0.87		
				0.475		1000	64.49		-0.12		
				0.461	2.60	1000	65.58	64.61	0.96	-0.01	7.58
8	1	1	1	0.485		1000	63.78		-0.83		
				0.499		1000	62.70		-1.92		
				0.486	1.63	1000	63.67	63.38	-0.95	-1.23	7.87

Table D -3 Lignin recovery results of aluminum electrodes at pH 6

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
1	-1	-1	-1	0.309		1000	47.36		1.07		
				0.304		1000	48.30		2.01		
				0.311	1.20	1000	47.11	47.59	0.82	1.30	6.44
2	1	-1	-1	0.274		1000	53.32		7.04		
				0.292		1000	50.26		3.97		
				0.271	4.07	1000	53.84	52.47	7.55	6.18	6.64
3	-1	1	-1	0.296		1000	49.66		3.37		
				0.273		1000	53.50		7.21		
				0.275	4.43	1000	53.15	52.10	6.86	5.81	6.89
4	1	1	-1	0.285		1000	51.45		5.16		
				0.289		1000	50.85		4.57		
				0.296	1.85	1000	49.66	50.66	3.37	4.37	6.86

Table D -3 Lignin recovery results of aluminum electrodes at pH 6 (con.)

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.321		1000	76.04		8.07		
				0.329		1000	75.44		7.48		
				0.322	1.35	1000	75.97	75.82	8.00	7.85	6.35
6	1	-1	1	0.221		1000	83.52		15.55		
				0.232		1000	82.66		14.69		
				0.236	3.42	1000	82.40	82.86	14.43	14.89	6.68
7	-1	1	1	0.319		1000	76.15		8.19		
				0.315		1000	76.45		8.49		
				0.314	0.84	1000	76.53	76.38	8.56	8.41	6.64
8	1	1	1	0.279		1000	79.18		11.21		
				0.239		1000	82.17		14.20		
				0.254	7.87	1000	81.05	80.80	13.08	12.83	7.19

Table D-4 Lignin recovery results of iron electrode at pH 8

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
1	-1	-1	-1	0.434		1000	26.07		-3.31		
				0.436		1000	25.81		-3.56		
				0.426	1.18	1000	27.43	26.44	-1.95	-2.94	8.17
2	1	-1	-1	0.452		1000	23.00		-6.37		
				0.424		1000	27.77		-1.61		
				0.434	3.26	1000	26.15	25.64	-3.22	-3.73	8.35
3	-1	1	-1	0.476		1000	18.91		-10.46		
				0.502		1000	14.57		-14.81		
				0.488	2.62	1000	16.96	16.81	-12.42	-12.56	8.30
4	1	1	-1	0.465		1000	20.79		-8.59		
				0.459		1000	21.81		-7.57		
				0.445	2.25	1000	24.20	22.26	-5.18	-7.11	8.67

Table D-4 Lignin recovery results of iron electrode at pH 8 (con.)

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.517		1000	61.39		-1.54		
				0.548		1000	59.07		-3.86		
				0.526	3.00	1000	60.68	60.38	-2.25	-2.55	8.22
6	1	-1	1	0.509		1000	61.95		-0.98		
				0.502		1000	62.51		-0.42		
				0.502	0.86	1000	62.51	62.33	-0.42	-0.60	8.30
7	-1	1	1	0.587		1000	56.12		-6.81		
				0.596		1000	55.49		-7.44		
				0.585	0.95	1000	56.27	55.96	-6.66	-6.97	8.25
8	1	1	1	0.521		1000	61.05		-1.87		
				0.540		1000	59.67		-3.26		
				0.559	3.52	1000	58.21	59.65	-4.71	-3.28	8.43

Table D -5 Lignin recovery results of iron electrode at pH 7

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
1	-1	-1	-1	0.343		1000	41.66		-0.90		
				0.369		1000	37.14		-5.41		
				0.369	4.21	1000	37.23	38.67	-5.33	-3.88	7.33
2	1	-1	-1	0.399		1000	32.12		-10.44		
				0.341		1000	42.00		-0.56		
				0.353	8.39	1000	39.87	37.99	-2.69	-4.56	7.55
3	-1	1	-1	0.330		1000	43.79		1.23		
				0.357		1000	39.27		-3.29		
				0.365	5.43	1000	37.48	40.18	-5.07	-2.38	7.58
4	1	1	-1	0.337		1000	42.68		0.12		
				0.365		1000	37.91		-4.65		
				0.378	5.89	1000	35.61	38.73	-6.95	-3.82	8.23

Table D-5 Lignin recovery results of iron electrode at pH 7 (con.)

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.458		1000	65.76		1.15		
				0.493		1000	63.18		-1.43		
				0.433	6.48	1000	67.63	65.53	3.02	0.91	7.28
6	1	-1	1	0.391		1000	70.77		6.16		
				0.432		1000	67.71		3.09		
				0.419	5.05	1000	68.72	69.07	4.10	4.45	7.47
7	-1	1	1	0.473		1000	64.68		0.06		
				0.489		1000	63.45		-1.17		
				0.441	5.22	1000	67.03	65.05	2.42	0.44	7.49
8	1	1	1	0.411		1000	69.31		4.70		
				0.408		1000	69.50		4.88		
				0.385	3.5	1000	71.22	70.01	6.60	5.40	7.97

Table D -6 Lignin recovery results of iron electrode at pH 6

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
1	-1	-1	-1	0.314		1000	46.60		0.31		
				0.300		1000	48.98		2.69		
				0.309	2.33	1000	47.36	47.65	1.07	1.36	6.39
2	1	-1	-1	0.300		1000	48.90		2.61		
				0.299		1000	49.07		2.78		
				0.300	0.19	1000	48.90	48.95	2.61	2.66	6.99
3	-1	1	-1	0.296		1000	49.58		3.29		
				0.297		1000	49.41		3.12		
				0.291	1.19	1000	50.51	49.83	4.22	3.54	6.72
4	1	1	-1	0.279		1000	52.47		6.18		
				0.282		1000	52.05		5.76		
				0.275	1.18	1000	53.15	52.56	6.86	6.27	8.32

Table D -6 Lignin recovery results of iron electrode at pH 6 (con.)

Experiment	Current density	Time	Initial solids content	UV absorption at 280 nm.	CV, %	Dilution	Lignin recovery, %	Average lignin recovery, %	Additional lignin recovery by electrochemical process, %	Avg. additional lignin recovery by electrochemical process,%	Final pH
5	-1	-1	1	0.331		1000	75.26		7.29		
				0.334		1000	75.03		7.07		
				0.337	0.82	1000	74.85	75.05	6.88	7.08	6.28
6	1	-1	1	0.299		1000	77.65		9.68		
				0.302		1000	77.42		9.46		
				0.301	0.50	1000	77.54	77.54	9.57	9.57	6.56
7	-1	1	1	0.318		1000	76.27		8.30		
				0.298		1000	77.72		9.76		
				0.333	5.47	1000	75.15	76.38	7.18	8.41	6.43
8	1	1	1	0.290		1000	78.32		10.35		
				0.300		1000	77.61		9.64		
				0.294	1.63	1000	78.06	78.00	10.09	10.03	7.44

APPENDIX E

CALCULATIONS

E-1: Lignin Concentration (LC) Calculation

LC, g/L= (UV absorbance value / 16.346) x dilution

Example Lignin concentration of original pH and water content

LC   = (0.533 / 16.346) x 2500

     = 81.5 g/L

E-2: Lignin Recovery (LR) Calculation

LR, % = [(Original LC- LC after electrochemical process)/ Original LC] x 100

Example Lignin recovery of preliminary test of aluminum electrode

LR, % = {[((0.533/16.346)x2500) - (0.474/16.346) x 1000)]/

         (0.533/16.346)x1000)} x 100

       = 64.43%

E-3: Additional Lignin Recovery by Acidification (ALR) Calculation

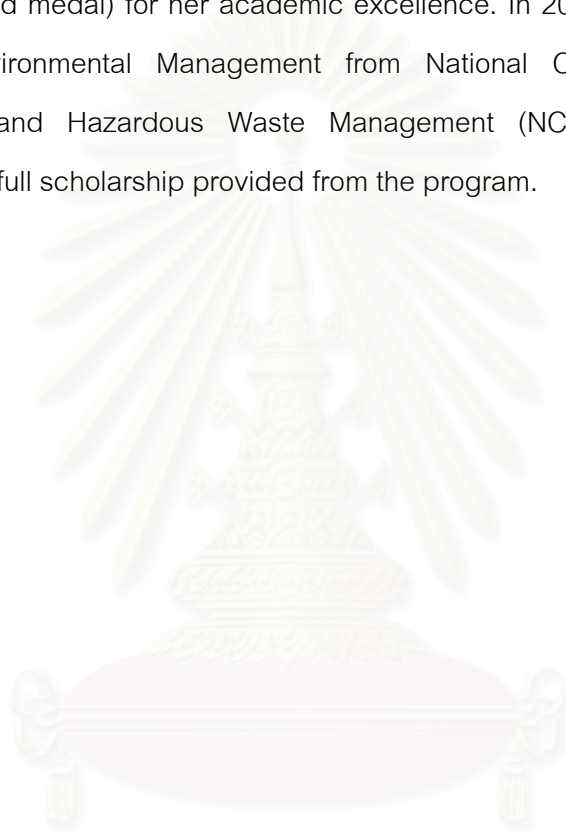ALR, % = LR by electrochemical process – LR by acidification

Example Additional Lignin Recovery by acidification of preliminary test of aluminum electrode

ALR   = 64.34% - 64.61%

      = -0.27 %

BIOGRAPHY

Sasivimon Chotinantasaeth was borned on October 8, 1982 in Bangkok, Thailand. She received her Bachelor's degree with first class honor with gold medal in Environmental Science, Major in Environmental Engineering from Sirindhorn International Institute of Technology (SIIT) Thammasat University in 2005. She also received Bhumipol Scholarship (gold medal) for her academic excellence. In 2008, she received Master's degree in Environmental Management from National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn Univerysity with full scholarship provided from the program.