Extraction of Lignin from Rubberwood with Alcohols and Microwave

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Abstract

Lignin is the most abundant phenolic polymers from nature, especially in biomass. Lignin derived phenolic compounds can produce high value liquid fuel. However, biomass mainly consists of cellulose, hemicellulose, and lignin. This project aims to study solvent extraction with microwave assisted method and to investigate the parameters involving in operation. In this experiment, rubberwood (*Hevea brasiliensis*) is selected as raw material because it is widely planting in Thailand. The lignin in rubberwood is extracted by using the solvent organic-base extraction with microwave assisted method. Ethanol and isopropanol are selected as solvent for lignin extraction. The wood and solvent are extracted in the microwave oven at the frequency of 2,450 MHz. The power of microwave (100 W and 200 W) and extracted time (5, 10, 15, 20, 25, and 30 min) are investigated parameters. The extracted lignin is analyzed by Fourier transform infrared (FT-IR). The result shows that the yield of extracted lignin increased when the extracted time and power of microwave are increased. Moreover, the yield from extraction with ethanol is higher than isopropanol. The highest yield of the extracted lignin is equal to 6.26% at condition of 30 min and 200 W when solvent is ethanol due to high lignin solubility. The total mass loss in this process is 16-25%, approximately. Besides, the result from FT-IR shows that the microwave can not only destroy the bond of lignin and other components, but it also destroys the ether bond of lignin.

Keywords: Delignification, Biomass deconstruction, Microwave

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บทคัดย่อ

ลิกนินเป็นสารที่ประกอบด้วยพอลิเมอร์ฟีนอลิกที่พบมากที่สุดในธรรมชาติโดยเฉพาะอย่างยิ่งในสารชีวมวล สารประกอบฟีนอลิกจากลิกนินสามารถแปรสภาพเป็นเชื้อเพลิงเหลวที่มีมูลค่าสูงได้ ในขณะที่ สารชีวมวลส่วนใหญ่ประกอบไปด้วย เซลลูโลส เฮมิเซลลูโลสและลิกนิน ในโครงงานนี้มีวัตถุประสงค์เพื่อศึกษาการสกัดด้วยตัวทำละลายโดยใช้คลื่นไมโครเวฟและเพื่อศึกษาตัวแปรต่าง ๆ ที่เกี่ยวข้องในการทดลอง ในการทดลองนี้เลือกใช้ไม้ยางพารา (*Hevea brasiliensis*) เป็นวัตถุดิบ เพราะว่าไม้ยางที่มีเพาะปลูกจำนวนมากในประเทศไทย และเป็นพืชเศรษฐกิจที่สำคัญ ลิกนินในไม้ยางพาราสกัดโดยใช้ตัวทำละลายอินทรีย์และคลื่นไมโครเวฟ ตัวทำละลายที่ใช้ในการสกัดลิกนิน คือ เอทานอลและไอโซโพรพานอล การสกัดลิกนินเกิดขึ้นในเตาอบไมโครเวฟที่ความถี่ 2,450 เมกะเฮิรตซ์ โดยใช้กำลังของไมโครเวฟที่ 100 วัตต์ และ 200 วัตต์ เวลาที่ใช้ในการสกัด คือ 5 10 15 20 25 และ 30 นาที ส่วนลิกนินที่สกัดได้จะถูกนำไปวิเคราะห์ด้วยเทคนิคฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโตรสโคปี (FT-IR) ผลการทดลองพบว่าปริมาณลิกนินที่สกัดได้เพิ่มขึ้น เมื่อเพิ่มเวลาและกำลังของไมโครเวฟในการสกัด นอกจากนี้ลิกนินที่ได้จากการสกัดด้วยเอทานอลนั้นมีปริมาณสูงกว่าการสกัดด้วยไอโซโพรพานอล ซึ่งลิกนินที่สกัดด้วยตัวทำละลายเอทานอลมีปริมาณสูงที่สุดเป็นร้อยละ 6.26 โดยใช้กำลังของไมโครเวฟ 200 วัตต์ เป็นเวลา 30 นาที เนื่องจากเอททานอลมีความสามารถในการละลายลิกนินที่สูงกว่า การสูญเสียมวลรวมในกระบวนการนี้อยู่ที่ร้อยละ 16 - 25 โดยประมาณ นอกจากนี้ผลจากฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโตรสโคปี แสดงให้เห็นว่า คลื่นไมโครเวฟไม่เพียงแต่สามารถทำลายพันธะระหว่างลิกนินกับส่วนประกอบอื่น ๆ แต่ยังสามารถทำลายพันธะอีเทอร์ระหว่างอนุพันธ์ของลิกนินได้

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Mr. Trakarn Yimtrakarn

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CHAPTER I
INTRODUCTION

1.1 Background

Industrial technology in the world is rapidly being grown increasing consumption of fossil fuel. However, fossil fuel is limited. For this reason, renewable energy becomes important role in alternative energy resources [1].

Biomass is renewable resource that comes from plant and animal. This energy can reduce the overall cost of energy and demand of fossil energy (biomass overall). Lignocellulosic biomass is a plant-base material consisting of cellulose (35 – 50%wt), Hemicellulose (20 – 35%wt), lignin (10 – 25%wt) and other components [2].

Lignin is aromatic heteropolymer that is synthesized from phenylpropanoid units and oxygenate chemicals. Moreover, lignin is a large source of aromatic substance from nature. Lignin can be transformed into a versatile applications, for example, lignosulfonate, copolymer/resin applications, metal ion absorption, and biofuel [3]. Rubber tree (*Hevea brasiliensis*) is a softwood that widely implants in Thailand. Furthermore, it is also important economics crop. Generally, softwood consists of cellulose and lignin higher than hardwood. From the above reason, rubberwood is selected in this research [4].

The lignin extraction from biomass can be carried on by delignification method. Chemical delignification methods are divided into two main solvents including aqueous and organic solvent-based [3]. In organic solvent-based method, alcohols are the most widespread used in organosolv process. Ethanol and isopropanol are selected as extraction solvent in this experiment. Since, advantages of alcohol solvents are eco-friendly, less hazardous, easily recovery, various application and easily diffuses into the wood [5].

Microwave technology is an alternative heating method of biomass. Microwave is dielectric energy that directly generates heat inside material. In contrast, other methods will generate heat by conduction [6]. This technique can reduce the operating time, increase yield of the product, save energy consumption and create heat distribution uniformly [7]. Furthermore, the previous researches indicated that after the biomass has been heated, the lignin in the wood are more extracted [8].

This research aims to extract the lignin from the rubberwood by using ethanol and isopropanol as solvent for further application. For example, the efficiency of sparking ignition engine will be enhanced by blending extracted lignin with gasoline. Furthermore, the lignin in the softwood contains coniferyl alcohol unit mainly and p-coumarin alcohol unit partly [9]. The performance of the engine may be improved from these compounds.

1.2 Objectives

1.2.1 To study solvent extraction of lignin from biomass with microwave assisted method

1.2.2 To investigate parameters involve in solvent extraction with microwave assisted method

1.3 Scope of work

1.3.1 Extract lignin from rubberwood using ethanol and isopropanol with microwave assisted method

1.3.2 Analyzing extracted lignin in this work using FT-IR spectroscopy and UV-visible spectrophotometer

1.4 Expected outputs

1.4.1 To be able to extract lignin from rubberwood

1.4.2 To be able to identify the function groups of extracted lignin

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Theory

2.1.1 Lignocellulose biomass

Lignocellulose biomass is a plant-base organic compound. The lignocellulose is composed of carbohydrate polymers (cellulose, hemicellulose) and aromatic compound (lignin). When the plant receives solar energy, it will convert carbon dioxide and water to form sugar (hexose) and oxygen by photosynthesis reaction as shown in Equation 2-1 [10] .The solar energy is transformed into chemical energy containing in biomass.

$$6CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (2\text{-}1)$$

Nevertheless, lignocellulose is the most abundant renewable fuel. The lignocellulose can be converted into usable energy sources by using chemical, physical, and biological processes. This energy sources are mostly used in terms of biofuel and biochemical [11].

Cellulose is a linear sugar polymer of D-glucose linked by β-1,4-glucoside bonds as shown in Figure 2.1. The degree of polymerization is up to 10,000 monomer units. In plants, cellulose appears in a cell system for strength of cell wall. This compound mostly uses to produce paper. Hydrolysis reaction converts cellulose to bioethanol which is valuable biofuel [11].

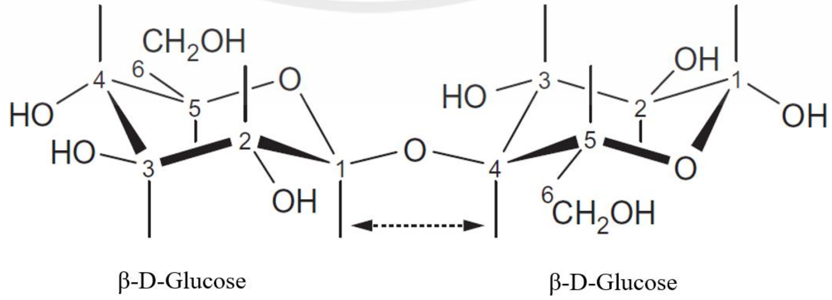


Figure 2.1 The fundamental unit of cellulose [10]

Hemicellulose is heteropolymers. Monomers in hemicellulose are glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid, and galacturonic acid residues. Generally, there are 500 – 3000 units connected branches. In addition, hemicellulose and cellulose present in cell walls together [11].

Lignin is second abundant resource in the world. For plant functional, lignin enhances mechanical strength properties of plant tissues, for instance, rigidity and hardness. The structure of lignin is randomly cross-linked of phenolic. Monomers mainly consist of three monomers including p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol as shown in Figure 2.2. The bond between each monolignol typically presents at the β-positions [9]. Figure 2.3 shows the linkages marked by solid squares are ether linkages, but the linkages marked by dot squares are condensed linkages [12].

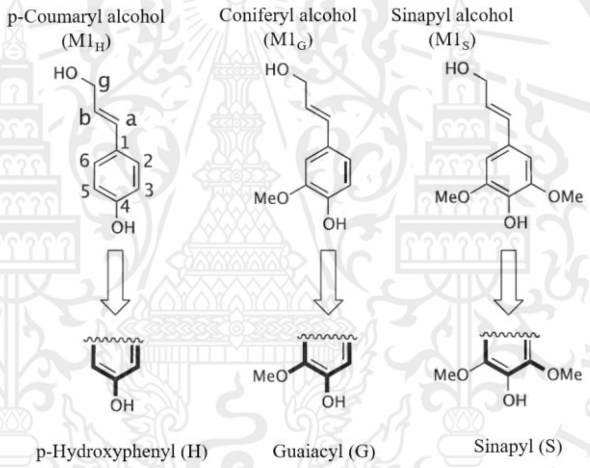


Figure 2.2 Monomers in lignin [9]

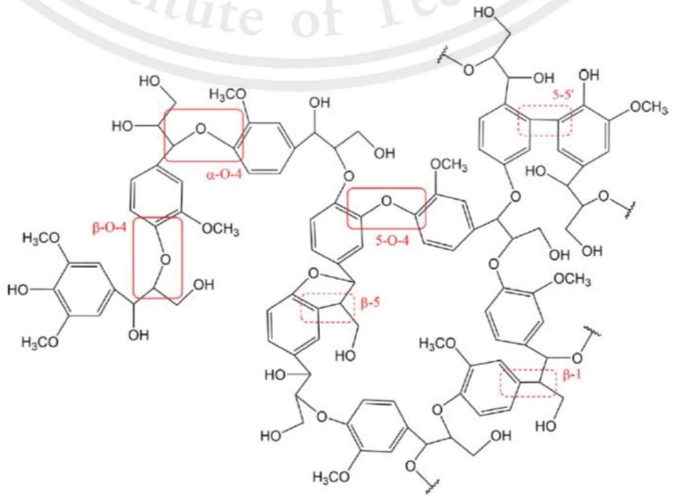


Figure 2.3 Several typical linkages within the lignin molecule [12]

Type of natural lignin can be classified according to two criteria that are plant taxonomy and the rate of basics phenolic units. Firstly, lignin is divided into three categories by plant taxonomy;

(1) Angiosperm lignins (hardwood plants)
(2) Gymnosperm lignins (softwood plants)
(3) Grass lignins (herbaceous plants).

This assortment has shown many exceptions from complexity of plant chemical structure. From this reason, the criteria have been developed to separate the lignin group by using the basics of phenolic units in the lignin. The new criteria consist of 4 groups;

(1) Type-G
(2) Type-G-S
(3) Type-H-G-S
(4) Type-H-G.

In the hardwood, monomers are coniferyl alcohol and sinapyl alcohol mainly (Type-G-S). Softwood monomer is Type-G or coniferyl alcohol mainly. For herbaceous plants lignin is basically Type-H-G-S. However, lignin monomers proportion depend on the specific nature of plants [9], as shown in Table 2.1.

Table 2.1 The proportion of lignin monomers in woods and herbaceous plants [9]

Type	**p-Coumaryl alcohol**	**Coniferyl alcohol**	**Sinapyl alcohol**
Softwood	<5%	>95%	0%
Hardwood	0% - 8%	25% - 50%	45% - 75%
Herbaceous plants	5% - 55%	35% - 80%	20% - 25%

Generally, softwoods contain 23 – 33% of lignin while hardwoods contain 16 – 25% of lignin. In addition, lignin presents good properties such a natural antioxidant, free radical scavenger, or it is the capacity to link to cations. The applications of lignin are more versatility processes to obtained high value product compounds. For example, lignin is combined with other substances to form a lignin-based biopolymer that has the antioxidant capacity or decomposed lignin to obtained vanillin. In construction field. lignin can be used as blinder by mixing with concrete to prevent lumping and settling of unsolved particles in suspension. The lignin can be transformed into an emulsifier for diesel-water fuel [13].

2.1.2 Separation method of lignin from wood

Several methods used for isolate lignin from wood. Separation of lignin is divided into three main categories depending on the technology used: chemical, physical, and biological, or a combination of them. In this section shown some separation technique such as lignin hydrolysis extraction, Brauns lignin, milled wood lignin, ethanol organosolv lignin, and thermochemical method.

2.1.2.1 Lignin hydrolysis extraction

Klason lignin is simple method and widespread in paper and pulp industry for isolated lignin from wood. The undesired material in the wood such as waxes, fats, some resin, and wood gum, are extracted by alcohol-benzene for cleaning and removal. Afterwards, 64 – 75% sulfuric acid is added for hydrolysis carbohydrate in cellulose. The hydrolyzed wood is introduced into water for acid dilution. Then, the mixture is boiled in water bath with reflux condenser. The mixture is left to set lignin settling down and filtrated black solid. Lignin appeared in black solid. The advantages of Klason lignin method are high accuracy and facile. In contrast, Klason method can change the structure of lignin throughout hydrolysis [14]. Another method is Willstatter lignin. Willstatter method is similar to Klason method. Whereas, hydrochloric acid is replaced by sulfuric acid [15].

2.1.2.2 Brauns or native lignin (BNL)

The wood is crunched in a Wiley mill. The 100 to 150 mesh screens are used for the selection of wood chip size. Wood chip is extracted by cold water, after that it would be extracted by ethyl ether for 48 hours to isolate the exterior component. Then, ethanol is added into solution at room temperature and leave for 8 to 10 days or until its color is clear. Calcium carbonate is added to neutralization pH of the solution. The alcohol is removed by the vacuum evaporator. Water is added to the residue. The evaporation is continuously operated to remove the amount of residues alcohol. Then, the lignin residue is grinded by pestle and mortar. After that, it is slowly added by water and anhydrous ether until it becomes solid. The solid is filtered by vacuum filter. Then, the liquid is dried by an efficient desiccant. The dried lignin is extracted by anhydrous ether in the soxhlet apparatus. The residue (aqueous) is dissolved by dioxane and becomes a 10% solution. Then, it is precipitated by dripping into stirred with distilled water (about 15 times the volume of the dioxane). The solution of lignin in ethanol is precipitated by the solvent until the methoxyl content is constant. Thus, this method got a yield of lignin around 8 percent of the wood. The advantage of Brauns or native lignin method gives minimally changes the structure of lignin. Characteristics of Brauns lignin are the same elemental compositions, low molecular weight lignin, large amounts of ester groups and higher phenolic hydroxyl content [16-17].

2.1.2.3 Milled wood lignin (MWL)

Bjorkman is found preliminary extensive grinding followed by solvents extraction method. The lignin from MWL method can be extracted a large portion of lignin. Firstly, the wood is treated by ethanol-benzene to remove extractive. After that, the wood introduced to vibration ball milling together with a solvent that non-swelling like toluene (at least 48 hours under nitrogen). The solvent that added into the vibration ball mill for extract lignin and reduced cake form on the milled ball. The next step is extraction with solvents. ball-milled wood is extracted twice by aqueous dioxane for 24 hours under the nitrogen atmosphere. The mixture is added by dropwise deionize water while stirring and freeze-dried. The freeze-dried crude is dissolved by 90% acetic acid and deionized water for precipitation of lignin. The solution is centrifuged to remove supernatant. The solid is dissolved by 1,2 dichloroethane/ethanol and precipitated in diethyl ether. The mixture is centrifuged. Then, solid washed twice with petroleum ether. Finally, the milled wood lignin is obtained. the yield of lignin is obtained about 50% of wood. Lignin presented in a white powder and containing some carbohydrate compounds [16, 18-19].

2.1.2.4 Organosolv lignin

The organosolv method is the most environmental and economical process. In addition, this method is simple process and solvent recycling possibilities. Organic solvents are used to extract lignin with acid/base as a catalyst. Organic solvent includes methanol, ethanol, propanol, butanol, isobutyl alcohol, acetone, benzyl alcohol, glycerol, glycol, ethylene glycol, triethylene glycol, phenol, acetic acid, formic acid, propionic acid, diethyl ether, amines, esters, ethers, formaldehyde and chloroethanol, among others, either in pure form or in aqueous solutions. For ethanol organosolv lignin, lignocellulose is treated with 35% ethanol with sulfuric at 190 °C for 1 hour. The treated sample is washed with 50 mL of aqueous ethanol three times. Then, 3 volumes of water are added to precipitate the lignin. After that, the ethanol organosolv lignin is centrifuged and dried. Organosolv lignin that obtained is low molecular weight, high phenolic and aliphatic hydroxyl contents [20-21].

2.1.2.5 Thermochemical method

External heating (pyrolysis) is the physical treatments that can degrade lignin. Increase in temperature affect to damage of chemical bonding. This method improves the depolymerization of lignin structure. Pyrolysis is a thermal process for treating organic compounds by limit oxygen. The organic compounds cannot convert to carbon dioxide without the oxygen. The condition of pyrolysis affects to lignin structure. Normally, lignin that is produced from this process give a low molecular weight of lignin fragments. If lignin is gasified at high temperature during the pyrolysis, the products become hydrogen, carbon dioxide, carbon monoxide, and methane. Therefore, the selection of temperature is important. At temperature between 150 – 400 °C, the products from depolymerization are usually the basic units of lignin, for example, 4-methylguaiacol, syringol, coniferyl alcohol, and some lignin-derived chemicals. At high temperature (higher than 450 °C), most of the linkages are cleaved to form o-vanillin, guaiacol, o-quinone methide, and lower molecular weight substances [12].

2.1.3 Techniques for characterizing lignin

Many techniques are available to characterize lignin. The techniques presented below consider only lignin contains in solution. Lignin is chemical structure and composition vary from source, type of lignin, and isolation method [22].

2.1.3.1 Ultraviolet-visible spectrophotometry

A UV-visible spectrophotometer is the most convenient and useful method for the quantitative and qualitative analyses of lignin in solution. Forasmuch, lignin is an aromatic structure base which greatly absorbs ultraviolet light. Although, this technique is not efficient for the defined structure of lignin.

In practice, spectrophotometer detects the intensity of light passing through a cuvette with a sample (I). Then, it compares to the intensity of light before it passes through the samples (I_o). the transmittance is the ratio I/I_o and presented as (%T). The absorbance (A) is calculated based on transmittance follow as the Equation (2-2) [23].

$$A = -\log\left(\frac{\%T}{100\%}\right) \tag{2-2}$$

The sample that suitable for the spectrophotometer is a liquid sample. Samples are prepared by dissolve in a solvent. However, a proper solvent is one criterion that must care to select. The spectrum of lignin may be changed by solvent effects. Proper solvents are water, ethanol, dimethylformamide, dioxane, pyridine, and dimethylsulfoxide (DMSO). In Figure 2.4, the aromatic nature of lignin presents at 280 nm is the result of a benzene ring substituted by hydroxyl or methoxyl groups [24].

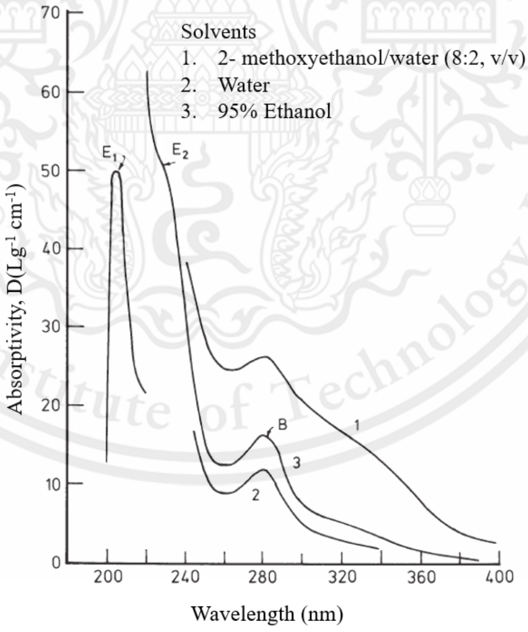


Figure 2.4 UV spectra of pine kraft lignin (1), spruce lignosulfonate (2), and milled wood lignin [24]

2.1.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy is used as an uncomplicated technique for obtaining quick and accurate results. In practice, FT-IR spectroscopy is an absorption technique that works when molecular vibration modes absorbing specific frequencies of the electromagnetic spectrum at varying intensities. IR spectroscopy electromagnetic radiation in the IR region is either transmitted through the sample or reflected off the surface. Resonant mode frequencies in the molecule are matched with IR photons that are absorbed. The emitted or absorbed radiation in the IR region is recorded. Wave numbers (υ, the number of waves per cm) are the radiation emitted in the IR region. FT-IR is good for characterized function groups in substance. Furthermore, the composition of lignin usually uses this method to find function group.

FT-IR spectrum of kraft lignin derived from a softwood (P. ponderosa). In the Figure 2.5 shows outstanding peaks that 3409 cm^{-1} (OH stretching), 1594 cm^{-1} (symmetric aryl ring stretching), 1512 cm^{-1} (asymmetric aryl ring stretching), 1463 cm^{-1} (asymmetric C-H deformation), 1266 cm^{-1} (aryl ring breathing), and 1030 cm^{-1} (aromatic CH in plane deformation).Their peaks are extremely presenting in lignin and can use for identified lignin [22 ,24].

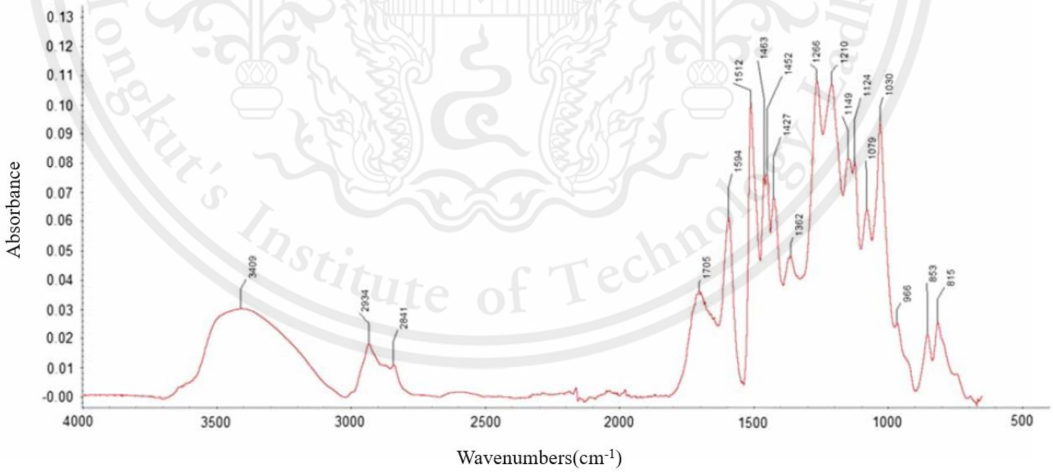


Figure 2.5 FT-IR spectra of a softwood kraft lignin derived from ponderosa pine [22].

2.1.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectroscopy can be used for the characterization and classification of lignin and determination of lignin structure. This technique magnetic field interacts with an atomic nucleus (e.g., the most common stable isotopes 1H, 13C, 15N) and radio frequency pulses to characterize the resonant frequency of that atomic nucleus according to its substance. This pulsed is changed to the spinning direction of the nucleus. This situation is an excited state during decay signal back or FID (free induction decay) to equilibrium. The signal is like an encrypted map of the chemical structure of molecules and polymers. In addition, difference molecules differ absorptivity. Though, the same molecule in unlike environmental surroundings are changed signals decay [22-23].

2.1.4 Oxygen bomb calorimetry

Calorimetry is the measurement for quantifying heat. Heat of combustion (calorific heat) is pervasively determined in an oxygen bomb calorimeter (Figure 2.6) [25].

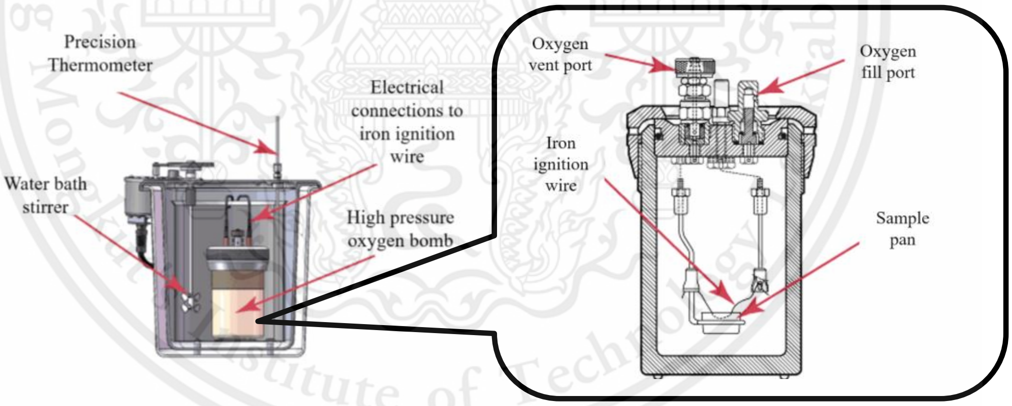


Figure 2.6 Oxygen bomb calorimeter and high pressure oxygen bomb [25]

The heat released by the combustion is absorbed within calorimeter which resulting in the changing temperature of absorbing medium [26]. The oxygen bomb calorimeter consists of high pressure oxygen bomb, absorbing medium and jacket. The vessel of high pressure oxygen bomb is made from thick metal which has screw cap for inserting sample. The bomb is placed in metal jacket that fill with absorbing medium or water. The sample is burned by iron ignition wire with 30 bars of oxygen supply. Therefore, the heat released from the system into the water after combustion is calculated from the increasing temperature of the water. The reaction of material combustion in bomb calorimeter at excess oxygen condition is shown in Equation 2-3.

$$C_xH_yO_z(s,l) + O_2(g) \rightarrow CO_2(g) + H_2O(l) \qquad (2\text{-}3)$$

The bomb calorimeter is a constant volume calorimeter. The heating value of the material is calculated by Equation 2-4,

$$q_{cal} = C_{cal}\Delta T = -q_{v,system} \quad \text{(J)} \qquad (2\text{-}4)$$

$$C_{cal} = C_{hardware} + m_{water}C_{s,water} \quad (\text{J/}^{o}\text{C}) \qquad (2\text{-}5)$$

$$q_{cal} = C_{hardware}\Delta T + m_{water}C_{s,water}\Delta T \quad \text{(J)} \qquad (2\text{-}6)$$

where q_{cal} = heat of calorimeter, J

$q_{v,system}$ = heating value of material, J

ΔT = change of water temperature, ^{o}C

m_{water} = mass of water, g

C_{cal} = heat capacity of the calorimeter, J/ ^{o}C

$C_{hardware}$ = heat capacity of hardware (stirring paddles, blades, the bomb, the wiring, the walls of the calorimeter, etc.), J/ ^{o}C

$C_{s,water}$ = specific heat of water, J/g/^{o}C

2.1.5 Heating value

The heating value of the fuel is defined as the amount of heat released from the complete combustion of the fuel. In other words, the heating value is equal to the absolute value of combustion enthalpy as shown in the Equation 2-4 [27].

$$Heating\ value = |h_c| \quad \text{(kJ/kg fuel)} \qquad (2\text{-}7)$$

The heating value depends on the phase of water in combusted product. The higher heating value (HHV) is the heating value when the water in the product is liquid form. The lower heating value (LHV) is heating value when the water in product is vapor form. The both of heating values are related to Equation 2-8 [27].

$$HHV = LHV + (mh_{fg})_{H_2O} \quad \text{(kJ/kg fuel)} \qquad (2\text{-}8)$$

where m = mass of water in the products per unit mass of fuel

h_{fg} = enthalpy of vaporization of water at the specified temperature, kJ/kg

2.1.6 Octane number

Octane number is a measurement of gasoline and other fuel to prevent knocking of sparking ignition engines. The high compression ratio engines are more prone to knocking, so the engines require high octane number fuel. In contrast, low compression ratio engines cannot completely work with high octane fuel. The compression ratio is fixed by engine design [28].

Gasoline that are suitable for the sparking ignition engines compose of lightweight hydrocarbons between 4 and 12 carbon atoms per molecule. However, the different structures of hydrocarbons cause interrupt ignition in the engine. Octane number specify the quality of gasoline. It is defined by compared to iso-octane and n-heptane. The octane number of iso-octane and n-heptane are 100 and 0, respectively. Moreover, the octane number does not correlate with energy in the fuel. It is only a measure of the fuel tendency to burn rather than explode.

The measurement method of octane number, the fuel is tested in a test engine with a variable compression ratio under controlled conditions. Then, it compares with mixtures of iso-octane and n-heptane.

2.1.7 Effect of microwave on biomass

The microwave can be an alternative method for heating instead of conventional heating. It has widely applied in the lignin and biomass thermochemical conversion. Microwaves are energy waves from the electromagnetic spectrum which frequencies ranging from 0.3 to 300 GHz. When the microwave passes through the material. There are converted to specific frequencies that can be absorbed by the material. The electric fields continue alignment and realignment of dipoles in polar liquids. While changing dipoles together with the migration of ions generates friction inside the material and makes internal energy. By comparison with conventional heating, microwave pass through the walls of heat container and the heat inside of the material directly. In contrast, heat from conventional heating is rought heat to inside material by convection and conduction. Thus, convectional heating is losing heat during conduction and convection. Generative heat from microwave is greater uniform than conventional method. In addition, microwave heating is better efficiency [6, 7].

Effect of microwave treatment on biomass, microwave heating is similar to the thermal effect on biomass. Increase in temperature and pressure are assisted in the disruption of lignin and cell walls. Moreover, microwave force dipoles to align with the oscillating electric field, working in the disruption of hydrogen bonds. The effects of microwave focus on the fractionation of lignocellulose. The radiation wave brake down the crystalline of cellulose molecules. The particle size of lignocellulose is decreased by radiation wave. As a result, increasing of lignocellulose surface area is easily diffused by a solvent. The fragmentation of lignocellulosic structure due to the thermal effects of microwave irradiation. Several studies found that the microwave irradiation enhancing the efficiency of delignification [29]. It also applies microwave technology to assist the isolation methods like pyrolysis, solvolysis, and hydrolysis with both alkaline and acid [7].

2.1.8 Microwave heating of organic solvents

Generally, microwave radiation at a frequency of 2450 MHz is commercial due to it avoids interference with telecommunication and cellular phone frequencies. Moreover, it has a significant effect on the rate of many processes in the chemical and food industry. On the other hand, the microwave can use in an extraction process. The energy at 2450 MHz is highly absorbed by water.

Materials that interact with microwaves divided into three categories

(1) Microwave reflected materials which are bulk metals and alloys, such as copper

(2) Microwave transparent materials such as fused quartz, borosilicate glasses, ceramics, Teflon, etc.

(3) Microwave absorbed materials such as aqueous solutions, polar solvent, etc. [30].

The rate of energy transfer in the microwave is evaluated by the strength of the field generated within the material that is irradiated, by the frequency of the radiation and by the loss factor. The dielectric constant (ε) indicates the capacity of the material to store energy from the applied field. The loss factor (ε") indicates the potentiality to dissipate this energy as heat. The dissipation factor (loss tangent, tan δ) is a ratio of the dielectric loss to the dielectric constant. The efficiency of material in converting microwave energy into heat can explain by the dissipation factor ($\frac{\varepsilon''}{\varepsilon}$). Generally, materials with higher ε and ε" values are faster heating rates than the material lower value. Moreover, the dielectric loss and the dielectric constant in the liquid phase have a higher value than other phases. And its decrease when the temperature of the liquid increases [31].

Microwaves transfer energy into materials by dipolar polarization, ionic conduction, and interfacial polarization. The mechanisms affect to rapid superheating of the materials (Figure 2.7). Commonly, the boiling of solvent at atmospheric is the point where the partial vapor pressure of the liquid is equal to ambient pressure.

However, the boiling point in microwave operation can higher than the normal boiling point. The microwave irradiation is dissipated over the whole volume of the solvent. The stable super-heated liquid generates infinitely small bubble from nucleation points. It makes high internal vapor pressure to resist the surface tension and the boiling point reach over normal boiling point. Hence, the solvent is super-heated [32].

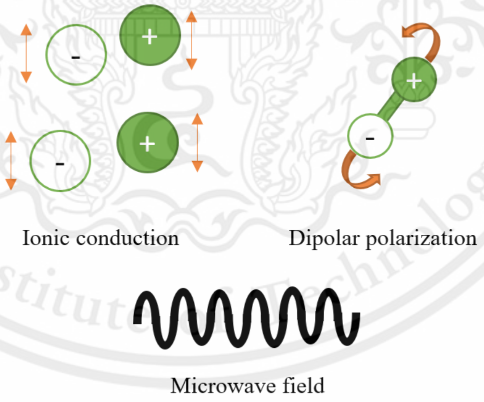


Figure 2.7 Ionic conduction and dipolar polarization under microwave conditions [32].

2.1.9 Rubber tree

The rubber tree (*Hevea brasiliensis*) is implanted for latex production in all tropical zones, especially in Southeast Asia and western Africa. In Southeast Asia, Thailand, Indonesia, and Malaysia are currently largest natural rubber producers. In Thailand, the rubber tree is cultivated the majority (68%) in the south of the country. The economic lifetime of rubber trees is 20–30 years for latex producing. Then, the old tree that has low latex production will annually cut for replanting. Normally, rubberwood is used to manufacture furniture, particle board, and plywood. Large branches produce charcoal. Nevertheless, small branches, stumps and roots are burned to prepare lands for replanting. Chemical composition in rubber tree, the rubberwood has consisted of cellulose (39 – 42%), hemicellulose (29 – 32%), and lignin (18 – 21%) [4, 33].

2.2 Literature review

An uncatalyzed ethanol organosolv pretreatment of softwood biomass, lignin and hemicellulose in softwood contains more chemical resistance when compared with hardwood. Thus, softwood requires more severe conditions for efficient separation. This process spends a long-time (120 – 240 minutes) and high temperature (160 – 220 ^{o}C). The highest yield of lignin is 51% at conditions of 220 ^{o}C, 196 min and 65% EtOH [34].

In the study of YU Hai-bo et al. [35], they extracted polyphenol from the grape peel with ethanol and microwave assisted method. The benefits of this technique are decrease in time, and oxidation prevention of polyphenols. Moreover, the microwave assisted method increases the yield of polyphenols.

Besides, Microwave was adapted in the delignification of biomass. In the study of Fanny, Monteil-Rivera [36], Biomass (triticale straw) was extracted by ethanol solvent extraction with microwave assisted. Microwave irradiations affect biomass increase the yield of lignin, more purity, and small molecular weight compared with conventional heating.

Saksit Imman [37] separated lignin containing in rice straw by solvothermal method. They studied the effect of solvent, acid promoters and microwave treatment. Thus, the results have shown that microwave assisted method compared to the conventional heating method. Microwave irradiation provides heat generated from the vibration of polar bonds in the biomass and surrounding solvent. Furthermore, microwave treatment appears higher reaction rate and shorter reaction time with better heat uniformly.

Dengle Duan et al. [38] performed microwave assisted acid pretreatment on pure lignin. They operate microwave conditions at 100 – 200 ^{o}C with 30 – 90 minutes. The microwave affects to the bonds of lignin. The vibration of bonds helps to break down the structure of lignin. Results showed that the increase in microwave temperature, time, can reduce the ash and oxygen content, and enhance the carbon content. Moreover, long microwave heating time can increase repolymerization reaction that is undesired to pretreatment.

In this experiment concern about moisture containment in extracted lignin. In addition, water can be making trouble in future utilization. For example, water is contaminated in the gasohol effect on decreasing efficiency and damaging in the engine. Phase separation of ethanol and gasoline may occur during high containment of water. When phase separation occurs in an ethanol blended gasoline, the water will actually begin to remove the ethanol from the gasoline [39].

CHAPTER III
RESEARCH METHODOLOGY

3.1 Materials and Apparatus

3.1.1 Materials

1. Rubberwood sawdust
2. Commercial grade organosolv lignin
3. Ethanol, 95% v/v
4. Isopropanol, 99.8% v/v
5. Sulfuric acid, 72% w/w
6. Distilled water

3.1.2 Apparatus

1. Microwave oven (SAMSUNG GE711K/XST Microwave (750W,20L,2450MHz))
2. Glass condenser
3. Universal oven (Memmert UN55)
4. FT-IR spectrometer (Nicolet i S20)
5. Oxygen bomb calorimeter (AC500)
6. UV-visible spectrophotometer (Thermo Evolution 201)
7. Quartz cuvette
8. 500 mL erlenmeyer flask
9. Buchner funnel
10. Suction flask
11. Filter paper Grade 42, 70mm Diameter (Whatman Biodegradable, Ash less)
12. Petri dish
13. 500 mL volumetric flask
14. 100 mL volumetric flask
15. 25 mL volumetric flask
16. Glass rod
17. Pipette

3.2 Experimental methods

3.2.1 Lignocellulosic biomass preparation

Rubberwood sawdust is kept in hot air oven at 105 ^{o}C for 24 hours for drying. Then, the material is kept in a beaker with plastic seal to avoid moisture until needed for lignin extraction.

3.2.2 Solvent extraction with microwave assisted method

The lignin extraction from biomass process is carried out in a 500 mL erlenmeyer flask. The 5 g of dried rubberwood sawdust (solid-to-liquid ratio of 1:10 by weight) is mixed with 95.6 % v/v ethanol or 99.8 % v/v isopropanol prepared in the room condition. The erlenmeyer flask is shaken and set up with modified microwave (Figure 2.1**)**. The condenser is closed with plastic seal. The solvent extraction with microwave assisted is performed in the microwave oven at the power of microwave (100 W and 200 W) and extracted time (5– 30 minutes with 5 minutes incremental). At the end of extraction, the weight of the flask is measured to determine the solvent that stuck in condenser. Then, solid fraction is separated from mixture by filtration on filter paper using a vacuum filtration set (Figure 2.2**)**. The solid residue is dried in the oven at 105°C within Petri dish. The difference weight of the residue solid after dried is measured. Subsequently, Weight of the liquid fraction is measured and collected data. The liquid solution is collected for further characterization. The mass loss in system is measured by the different of glassware weight before and after used.

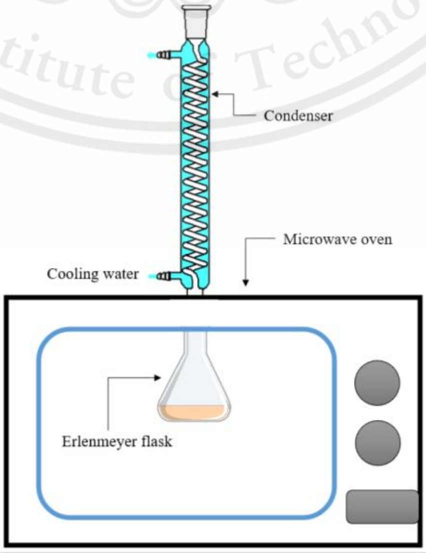


Figure 3.1 Schematic of the microwave oven

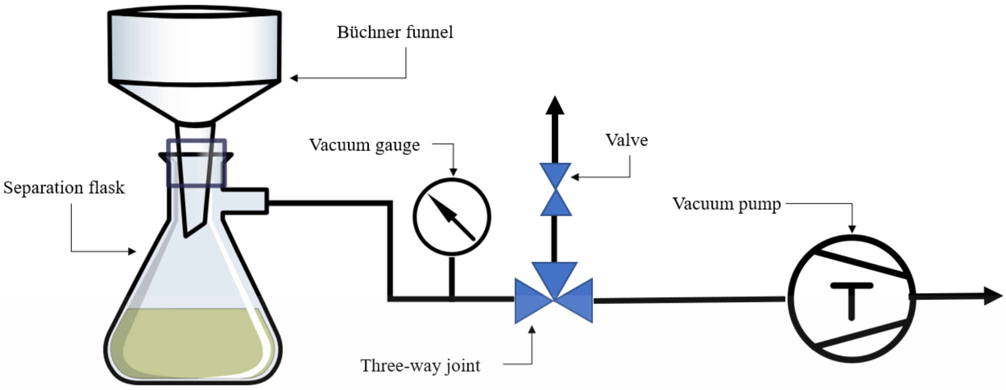


Figure 3.2 Schematic of the vacuum filtration set

3.2.3 Klason lignin extraction

1 g of dried wood is hydrolyzed by 15 mL of 72% sulfuric acid and stirred with a glass rod. After the specimen dispersion, the beaker is covered with watch glass and kept in a water bath for 2 hours. Then, 300 – 400 mL of water is added into 1000 mL flask. The material in the beaker is transferred to the flask. The solution is diluted by rinse water to a total volume of 575 mL. The mixture is boiled in the reflux system to maintain its volume for 4 hours. Lignin is precipitated by keeping the flask at the inclined position for 12 hours. Then, the solution is filtrated by vacuum filtration and washed acid remaining in precipitated lignin by using hot water. The filtration paper with lignin is kept in oven at 105 ^{o}C for 24 hours. Finally, the lignin in the dried wood (Klason lignin) is calculated by Equation 3-1 [40].

$$\text{Lignin \%} = A\ 100 / W \tag{3-1}$$

where Lignin % = lignin content in wood sample
A = weight of lignin, g
W = dry weight of test specimen, g

3.3 Characterization and quantification of lignin

3.3.1 UV-visible spectrophotometer analysis

The solution samples are analyzed using a UV-visible spectrophotometer. 0.3 mL of lignin sample is dissolved in 2.7 mL 95.6 % v/v ethanol in quartz cuvette. Then, the sample absorbance is recorded at the wavelength of 200 – 400 nm.

3.3.2 Standard curve

To create the lignin standard curve, 0.25 g of commercial lignin is added into 95.6 % v/v ethanol in 100 mL of volumetric flask. Then, 20, 10, 5 mL of the prepared solution is pipetted into each 25 mL of volumetric flask and followed by adding 95.6 % v/v ethanol into the volumetric flask. The solution samples are analyzed using a UV-visible spectrophotometer. 0.3 mL of lignin sample is dissolved in 2.7 mL 95.6 % v/v ethanol in quartz cuvette. Then, the sample absorbance is recorded at the wavelength of 280 nm. The standard curve is plotted to show the relation between concentration and absorbance of standard sample.

3.3.3 Yield of extracted lignin

The weight of extracted lignin is determined by UV-visible spectrophotometer comparing with standard curve. The total lignin in rubberwood is determined by Klason method. Total lignin contain in the wood shows in Appendix D. Yield percentage of extracted lignin is calculated by Equation 3-2

$$\%Yield_{Lignin} = \frac{W_{ExtractedLignin}}{W_{TotalLignin}} \times 100\% \tag{3-2}$$

where $W_{\text{Extracted lignin}}$ = weight of lignin extracted
$W_{\text{Total lignin}}$ = weight of lignin present in feedstock

3.3.4 FT-IR spectroscopy analysis

Lignin solution from extraction pour in 100 mL beaker. The beaker is heated in fume hood by hot plate at 75°C for ethanol (85°C for IPA) until the solution become half dry. Then, the liquid remaining is dried in the vacuum oven at 105°C within Petri dish for 24 hours. The prepared sample are inspected by ATR technique. FT-IR data that is analyzed from Sci-Ins, King mongkut's institute of technology ladkrabang is measured on the Nicolet iS20 FT-IR Spectrometer. The data recorded with 4 cm^{-1} spectral resolution per sample. Moreover, the spectra are in the range of 4000 to 700 cm^{-1}.

3.3.5 Bomb calorimeter analysis

20-50 mL of extracted solution is prepared in the stainless-steel vessel with oxygen supplied. The vessel containing the solution sample is inserted into the calorimeter, with temperature ranging from 18 °C to 24 °C. The higher heating value (HHV) that is analyzed from STREC, Chulalongkorn university is measured on the LECO AC500 Isoperibol calorimeter.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of solvent and microwave power on yield of lignin

In Figure 4.1 shows % yield extracted lignin from deconstructed biomass in microwave oven by using different solvents at various time and power of microwave. The yield extracted lignin increased with increasing of extraction time and microwave power. In addition, lignin that is extracted by ethanol is higher yield of extracted lignin comparing with isopropanol. The effect of solvent, the microwave power and extracted time are discussed in further sub-heading.

4.1.1 Effect of solvent

Figure 4.1 shows the relation between % yield extracted lignin and extraction solvents at various time and power. The lowest % yield extracted lignin is observe at isopropanol as solvent. Due to lignin has low solubility capacity in the isopropanol. Ethanol is more effective than isopropanol with high speed of delignification. Ethanol shows higher extracted lignin even at 100 W. Since, primary alcohols provide more selective delignification than the secondary and tertiary alcohols [41]. Moreover, ethanol has a lower molecular weight that is accommodated to provide higher permeability and fluidity [42]. Alcohols have hydroxyl group that is nucleophilic reactive functionalities. Alcohol can decompose the glycosidic bond in cellulose and ether bond in lignin [43]. The highest lignin concentration shows at condition microwave power at 200 W for 30 minutes with ethanol as solvent. Besides, isopropanol gave low yield of extracted lignin at the maximum yield at only 2.72 % while the ethanol gave lignin yield at 6.26 % at the same condition. Although, isopropanol can reach the maximum temperature higher than ethanol in microwave, but the solubility capacity is more essential influence.

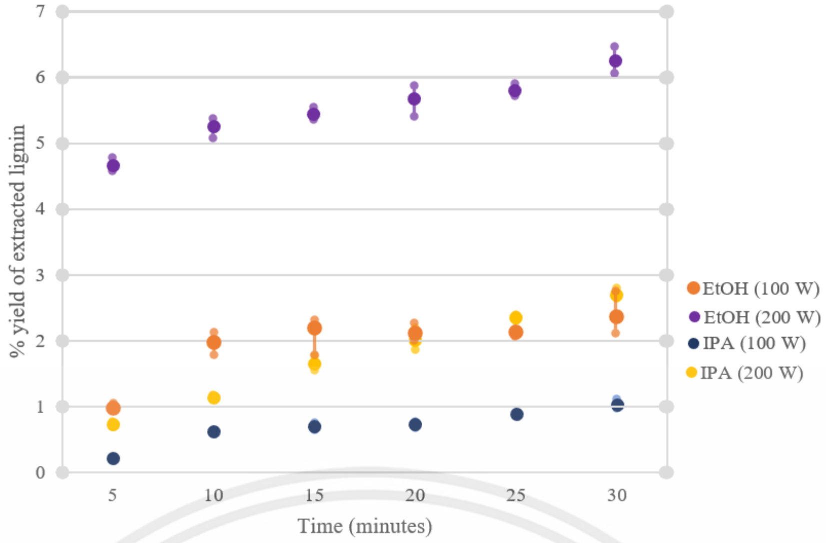


Figure 4.1 % Yield of extracted lignin

4.1.2 The microwave power and extracted time

The operating power is direct variation to temperature. The power of microwave effects on boiling point of solvent. The alcohols (ethanol and isopropanol) are low-boiling point solvent. During extraction in the microwave, the boiling point can exceed atmospheric boiling point [32]. Besides, this experiment can not measure the temperature inside oven because temperature measurement of microwave oven must use fiber optic thermocouple or internal IR sensor. Farid Chemat and Erik Esveld reported the boiling point of ethanol 20 mL reached over normal boiling point around 12 kelvins during microwave operating at 100 W [32]. Figure 4.2 shows the influence of the microwave power on superheating effect. Thus, the operating temperature with microwave higher than conventional heating.

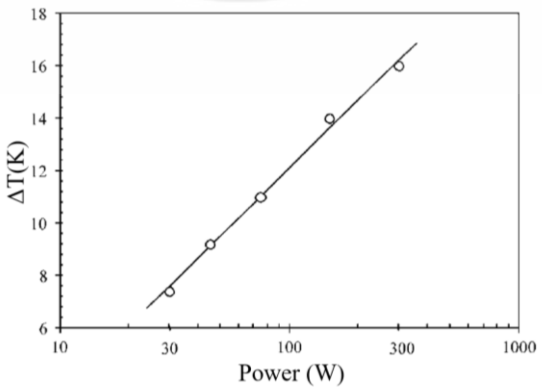


Figure 4.2 Effect of microwave power (20 mL of ethanol) [32]

Commonly, the solubility increases with temperature. The solubility of lignin in the solvent increases from increasing of microwave power. Moreover, the increment in temperature reduces the viscosity and improves the diffusivity of the alcohol solvent. It promotes effective interaction between lignocellulose and solvent. For this reason, the lignin yields are increased by increasing power of microwave [44]. Increasing of microwave power from 100 W to 200 W significantly increased the lignin yield in range of 2.38% – 6.26% in ethanol solvent at 30 minutes. Yield of lignin in isopropanol also increased 1.05 to 2.72 % at the same extracted time. The effect of extracted time, at short extracted time (5 minutes) has low yield lignin because the low extracted time is low reaction temperature. This period is not enough to break the strong bond between lignin and the other component. Thus, the increasing of time enhances lignin yield and efficiency of depolymerize of biomass. The yield of extracted lignin by this method is lower than the organosolv method. However, lignin extracted by organosolv method causes waste from acid or alkaline catalyst. While the advantage of another method, is absence of acid, or alkaline catalysts during processing.

4.2 Mass loss

In this experiment determined mass loss in extraction process, loss trapped in glassware, loss in filtration process, and loss during pulp drying. Mass loss during extraction process is observed for checking the efficiency of condenser in extraction process. The highest mass loss is found during the filtration process. The total mass loss in process shows in Figure 4.3. Total mass loss in this process in range 16% – 25%. Ethanol shows higher mass loss because it is more volatile solvent than isopropanol.

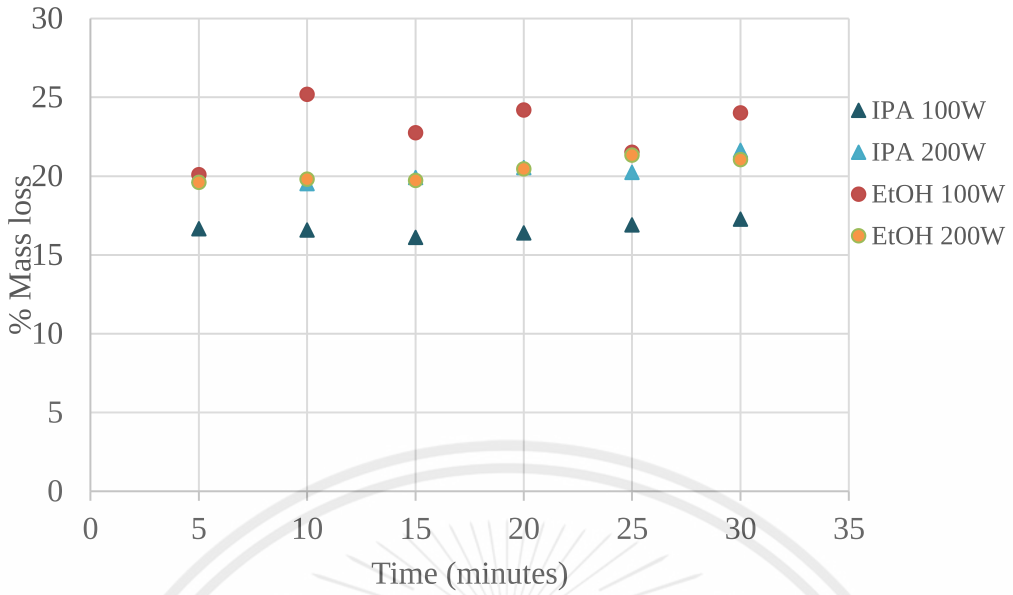


Figure 4.3 Percentage of total mass loss in process

Figure 4.4 shows % mass loss of solvent at various extracted time and microwave power. Mass loss slightly increased when expanded microwave power and extracted time. The power of microwave can increase the maximum temperature of the solvent. So that, the evaporation rate is increased at high power. At microwave power 100 W, initial period (5-10 minutes) of isopropanol shows lower solvent evaporated than ethanol because isopropanol has lower loss tangent value (Tan δ). The loss tangent indicates the heating rate. In contrast, ethanol that higher loss tangent value quickly rises the temperature. Loss tangent of isopropanol is 0.799. Besides, loss tangent of ethanol is 0.941. Isopropanol has higher maximum temperature resulting in higher evaporation rate than ethanol solvent. Ethanol loss during extraction process is in range 0.90 – 1.37%. Isopropanol loss during extraction process is in range 0.35 – 2.73%. The microwave oven that connected with a condenser is designed for recovery of solvent evaporation. Mass loss during extraction that may be solvent that struck in the condenser. However, the condenser shows a good recovery that has evaporation of solvent not above 3%.

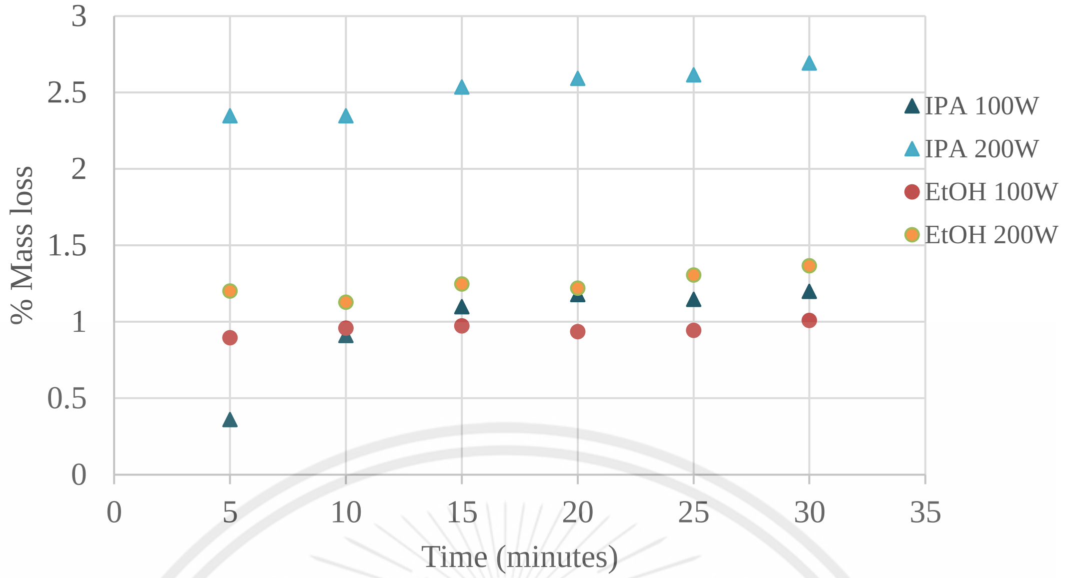


Figure 4.4 Percentages of mass loss during extraction process

Figure 4.5 shows the percentage of mass loss in further steps of experiment. Mass loss in solvent trapped inside glassware (erlenmeyer flask, Buchner funnel and suction flask), mass loss during filtration process, and loss during pulp drying are not significant difference. These are unavoidable and uncontrollable mass loss. Mass loss in solvent trapped inside glassware is around 3.30% – 3.96 % in ethanol as solvent and 2.30% – 3.31% in isopropanol as solvent. Mass loss in filtration process is around 8.30 – 10.84% in as ethanol solvent. While isopropanol that is extracted solvent evaporated around 6.82% – 9.35%. Ethanol remaining in solid residue is in range 7.49 – 7.79%. and isopropanol remaining in solid residue is in range 5.33% – 6.58%.

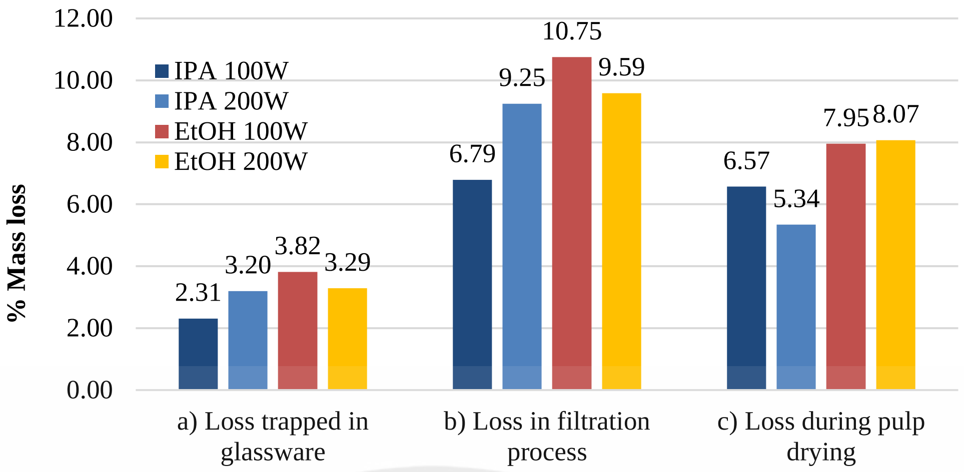


Figure 4.5 Percentages of mass loss a) loss trapped in glassware b) loss in filtration process c) loss during pulp drying

4.3 Characterization of extracted lignin

4.3.1 FT-IR spectroscopy analysis

Figure 4.6 shows the FT-IR spectra of lignin isolated from this experiment. Table 4.1 shows list of major peaks in FT-IR result. is also reported. The FT-IR spectra of products are compared with the commercial organosolv lignin and Klason lignin from rubberwood [24, 37, 42, 45-46].

FT-IR results, the spectra of extracted lignins that are extracted by isopropanol and ethanol have not significant difference. Besides, the Klason and Organosolv method are not exactly same with the sample from this extraction. The board band at 3680-3025 cm^{-1} is the O-H stretching vibration in the aromatic and aliphatic OH groups. At 3680-3025 cm^{-1} , The extracted lignin using isopropanol as solvent achieves a higher relative intensities indicating that the higher hydroxy group content in solution. Moreover, the lignin from Klason and organosolv that using acid as catalyst have lower oxidation comparing with this method. Bands at 2930 cm^{-1} and 2850 cm^{-1} are CH stretch in methyl and methylene group and C–H stretch in O–CH3 group, respectively. The peak at 1716 cm^{-1} is C=O stretch of unconjugated ketone, carboxyl, and ester groups which can be used to investigate the lignin and remaining hemicellulose during the extraction. The peak at 1660 cm^{-1} is assigned the conjugated carbonyl stretching in lignin. The peaks at 1600, 1510, 1170, and 1420 cm^{-1} are aromatic skeletal vibrations and the C-H deformation combined with aromatic ring vibration at 1455 cm^{-1}. There peaks in the Klason and organosolv lignin show clearer peak because these methods have precipitation of lignin in the water. In contrast, this method must beware the moisture content in the solution. The absorbance at 1368 cm^{-1} represents the phenolic hydroxyl group which can be attributed to the cleavage of β-O-4 bonds during extraction. This band is indicating that the microwave irritation not only break the bond connecting lignin with cellulose and hemicellulose but also break ether bond in the lignin. The peaks at 1265, 1226 and 833 cm^{-1} correspond to guaiacyl units. The guaiacyl (Coniferyl alcohol) is the highest monomer content in lignin from rubberwood. The absorbance at 1325 and 1126 cm^{-1} is Syringyl ring breathing and C–O stretching. The absorbances at 1026 is assigned to the C–O–C mode of the glycosidic linkages. This absorbance at 1026 cm^{-1} is indicated the glycosidic of cellulose and hemicellulose are remaining in the solution. 925 cm^{-1} is indicated pyranose ring in hemicellulose. The solutions from both solvent extractions contain with rich of phenolic, carbonyl, and aromatic compound. The spectra identified that the samples composed with lignin. However, the samples are contaminated with cellulose and hemicellulose that remained during extraction.

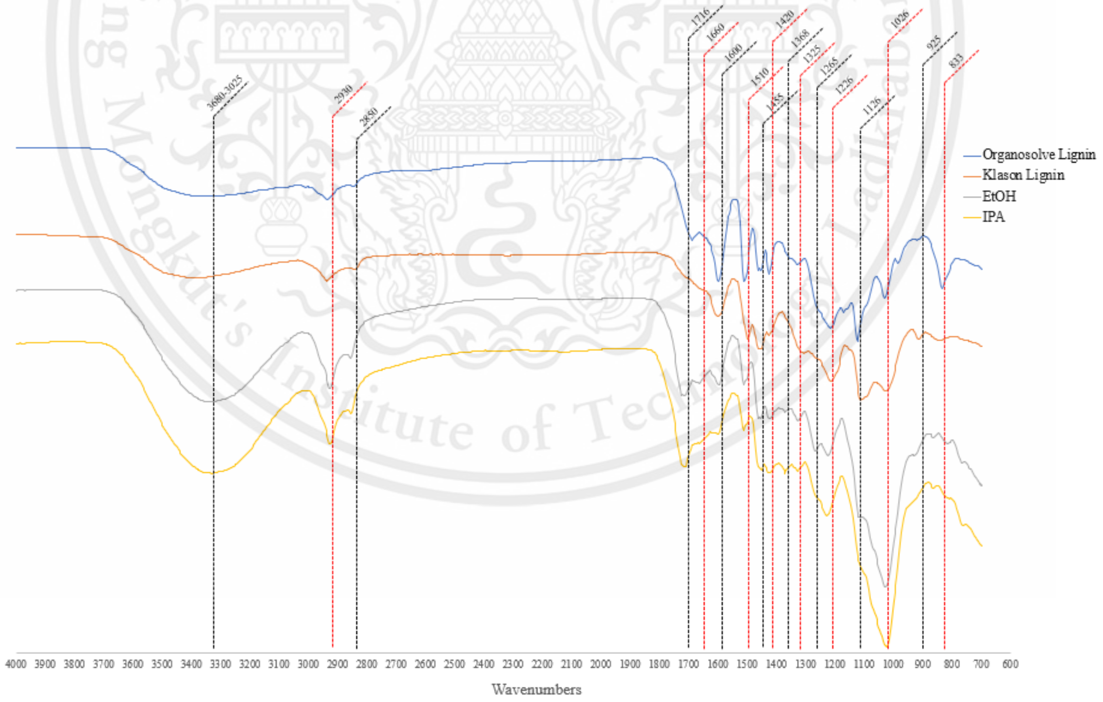


Figure 4.6 FT-IR spectra of lignin by organosolv, Klason, and microwave assisted method

Table 4.1 Assignment of FT-IR bands [20, 37, 45, 47]

Wavenumbers (cm^{-1})	Assignments
3680-3025	O–H stretch, H-bonded
2,930	C–H stretch methyl and methylene groups (aliphatic)
2850	C–H stretch O–CH3 group
1716	C=O stretch, unconjugated ketone, carboxyl, and ester groups
1660	C=O stretch conj.
1600	Aromatic squel vibration
1510	Aromatic squel vibration
1455	CH deformations and aromatic ring vibrations
1420	Aromatic skeletal vibration combined with C–H in plane deformation
1368	Phenolic hydroxyl group
1325	Syringyl ring breathing, C–O stretch
1265	C–C, C–O, and C=O stretches in Guaiacyl
1226	Guaiacyl ring breathing
1170	Aromatic C–H in plane deformation
1126	Syringyl ring breathing
1026	C-O-C
925	C–H deformation of out of plane, aromatic ring, pyranose ring
833	Aromatic CH out of plane deformation G + S

4.3.1 UV-visible spectrophotometer analysis

The UV spectra of products are shown in Figure 4.7. Lignin solutions present UV spectra characteristic of lignin with the maximum peak at 280 nm with indicated the non-conjugated phenolic in softwood lignin [24, 48]. The Klason lignin is used for comparing with lignin solution from experimental method. The extracted lignin solutions form both solvents shown maximum peak at 280 nm same with Klason lignin. In addition, the absorbance of the extracted lignin by isopropanol is lower than ethanol as solvent at same condition. This result indicated ethanol solvent has high extract efficiency. In extracted solution by isopropanol, the absorbance at 208 indicated isopropanol absorption.

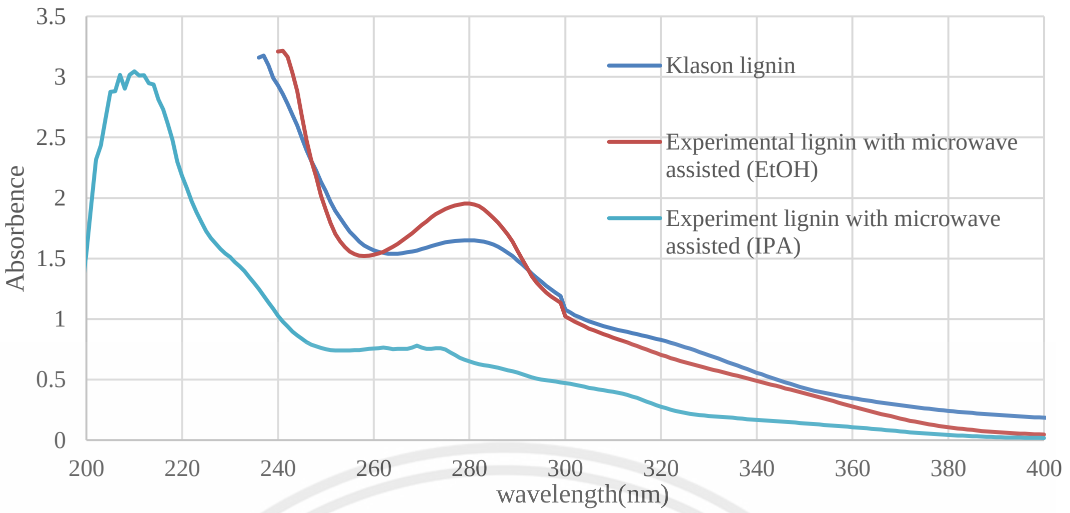
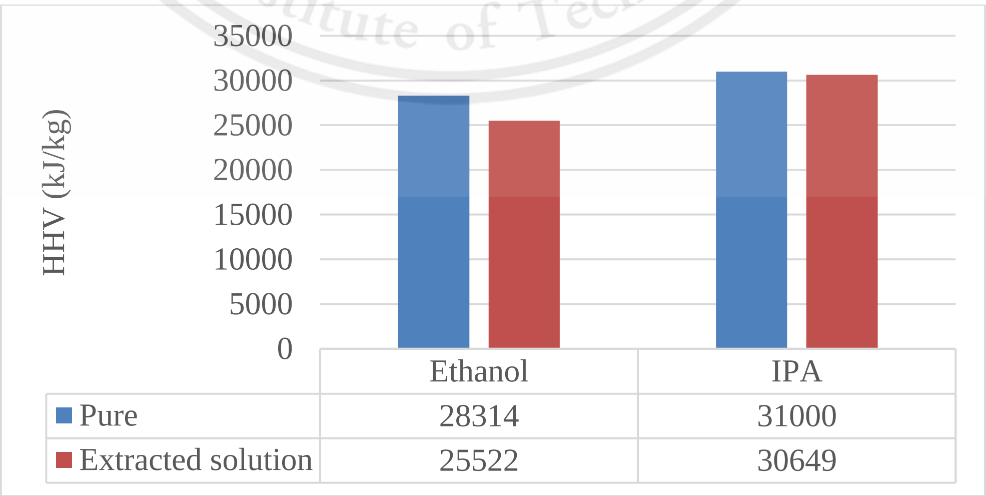


Figure 4.7 UV-visible spectra of experimental lignins and Klason lignin

4.3.2 Heating value analysis

Figure 4.8 shows higher heating value (HHV) of the extracted solution compared with pure solvent (95.6 % v/v ethanol and 99.8 % v/v isopropanol). The extraction condition of extracted solutions is selected at microwave power of 200 W and 30 minutes. HHV of both extracted solutions are lower than pure solvent. HHV of lignin (17000 – 25000 kJ/kg) depends on molecular weight of lignin [49]. In addition, the heating value of lignin is lower than the pure alcohol solvent. The HHV of the extracted solution by using ethanol as a solvent is less than 9.86% compared with ethanol 95%. The HHV of the extracted solution by using isopropanol as a solvent is less than 1.13% compared with isopropanol.



	Ethanol	IPA
🟦 Pure	28314	31000
🟥 Extracted solution	25522	30649

Figure 4.8 Higher heating value of extracted solution and pure solvent

In the last part of this experiment, the solvents and the extracted solutions are burned in cylindrical aluminum container at room conditions. The feature of each container after burning are shown in Figure 4.9. It shows that the yellow stain is appeared in the container of the extracted solutions (A and C) after burning. Since the extracted solutions consist of aromatic function in their structure. Therefore, they require oxygen more than the solvents for complete combustion [27]. However, the extracted solutions should be blended with gasoline. Then, the mixture should be test in spark ignition engine to determine the engine efficiency and octane number.

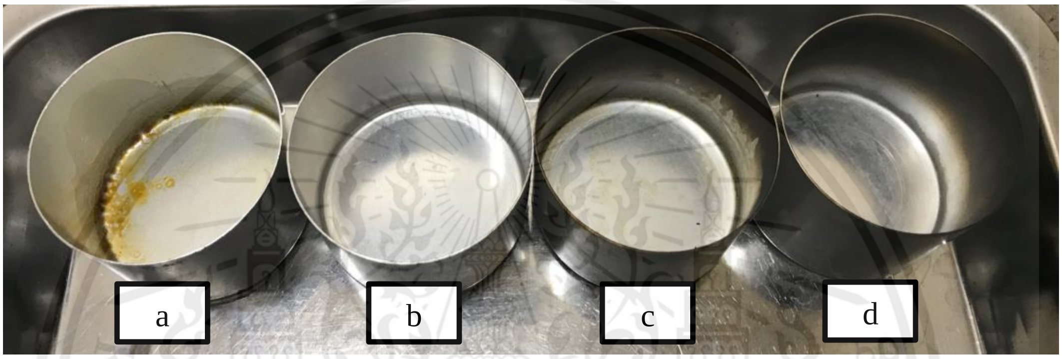


Figure 4.9 The cylindrical aluminum container after burning a) the extracted solution by using ethanol as a solvent b) ethanol 95% c) the extracted solution by using isopropanol as a solvent d) isopropanol

CHAPTER V

CONCLUSIONS

5.1 Conclusions

In this research, it is expected to study extraction of lignin by using solvent extraction with microwave assisted method. In this experiment, operating time and power of microwave are selected for finding suitable conditions. The results indicate that, ethanol extraction has more effective than isopropanol with high lignin solubility. The yield of extracted lignin recovery increased with increasing operating time and power of the microwave. The highest lignin recovery yield is 6.26 % at condition 200 W, 30 minutes, and ethanol as solvent. The total mass loss in this process is around 16 - 25 %. The microwave irritation breaks the bond connecting lignin with cellulose and hemicellulose. The ether bond that connect the lignin monomer is broken by microwave. In addition, the extracted of lignin is contaminated with hemicellulose and cellulose because this process does not have precipitation of lignin in water. The heating value of extracted solutions are lower than pure solvent due to low heating value of lignin.

5.2 Suggestions

1) Operating conditions including microwave power and extraction time should be increased to enhance the yield of lignin.
2) An extracted lignin in this research needs further analysis.
3) Organosolv experiment should be done.

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APPENDIX

Appendix A Properties of materials

1A Ethanol

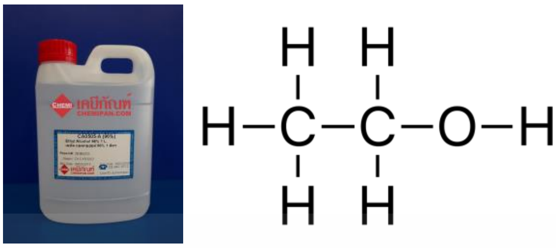

Figure A.1 Ethanol and its chemical structure

Table A.1 Properties of ethanol

Properties	**Value**	**Unit**
General Name	Denatured Ethanol	
Purity	95.6 % v/v	
Hazardous (NFPA 704)		
Molar mass	46	g/mol
Boiling point	78.2	°C
Specific gravity (20ºC)	0.800	
Solubility (δ)	12.9	$cal^{0.5}cm^{-1.5}$
Dielectric constant(ε´)*	24.3	
Dielectric Loss(ε´´)*	22.866	
Tan δ*	0.941	
Higher heating value	28,314	kJ/kg
Lower heating value	25,076	kJ/kg

*Dielectric constant(ε´), Dielectric Loss(ε´´) and Tan δ (measured at room temperature and 2450 MHz)[50]

2A Isopropanol

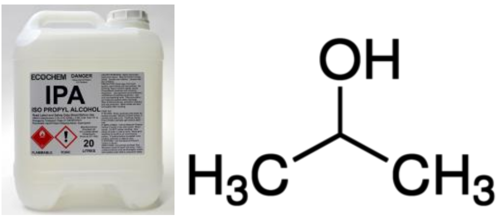

Figure A.2 Isopropanol and its chemical structure

Table A.2 Properties of isopropanol

Properties	**Value**	**Unit**
General Name	Isopropyl alcohol	
Purity	99.8 % v/v	
Hazardous (NFPA 704)		
Molar mass	60	g/mol
Boiling point	81.4	°C
Specific gravity (20ºC)	0.786	
Solubility (δ)	11.6	$cal^{0.5}/cm^{1.5}$
Dielectric constant(ε´)*	18.3	
Dielectric Loss(ε´´)*	14.622	
Tan δ*	0.799	
Higher heating value	31,000	kJ/kg
Lower heating value	30,451	kJ/kg

*Dielectric constant(ε´), Dielectric Loss(ε´´) and Tan δ (measured at room temperature and 2450 MHz)[50]

3A Sulfuric acid

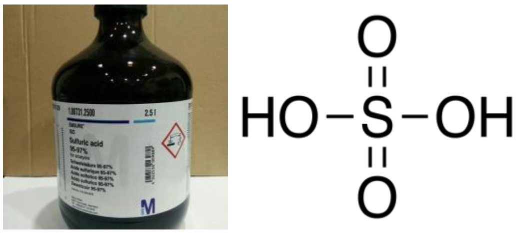

Figure A.3 Sulfuric and its chemical structure

Table A.3 Properties of sulfuric acid

Properties	**Value**	**Unit**
Chemical formula	H_2SO_4	
Purity	95-97 % v/v	
Hazardous (NFPA 704)		
Molar mass	98	g/mol
Boiling point	337	°C
Specific gravity (20°C)	1.830	

3A.1 Preparation of sulfuric acid 72%

66.5 mL of concentrated sulfuric acid 95-97% pour into 30 mL of water. Then, the solution is cooling in water bath and make up to 100 mL. the acid is cooled before using.

Appendix B Raw data of the extracted lignin absorbance, concentration, and % yield

Raw data of the extracted lignin absorbance, concentration, and % yield

Table B.1 Raw data of the extracted lignin absorbance, concentration, and % yield

No.	Solvent	Power (W)	Time (min)	Absorbance at 280 nm.	Concentration (g/100ml solution)	% Yield
1	EtOH	100	30	0.793	0.045	2.762
2	EtOH	100	30	0.660	0.038	2.267
3	EtOH	100	30	0.617	0.035	2.127
4	EtOH	100	25	0.632	0.036	2.187
5	EtOH	100	25	0.595	0.034	2.066
6	EtOH	100	25	0.624	0.036	2.167
7	EtOH	100	20	0.577	0.033	2.004
8	EtOH	100	20	0.603	0.035	2.095
9	EtOH	100	20	0.654	0.037	2.273
10	EtOH	100	15	0.512	0.029	1.784
11	EtOH	100	15	0.723	0.041	2.505
12	EtOH	100	15	0.670	0.038	2.329
13	EtOH	100	10	0.573	0.033	2.012
14	EtOH	100	10	0.610	0.035	2.135
15	EtOH	100	10	0.512	0.029	1.792
16	EtOH	100	5	0.304	0.017	1.050
17	EtOH	100	5	0.274	0.016	0.948
18	EtOH	100	5	0.282	0.016	0.976
19	EtOH	200	30	1.765	0.101	6.139
20	EtOH	200	30	1.798	0.103	6.253
21	EtOH	200	30	1.857	0.107	6.468
22	EtOH	200	30	1.747	0.100	6.071
23	EtOH	200	25	1.700	0.098	5.908
24	EtOH	200	25	1.649	0.095	5.721
25	EtOH	200	25	1.677	0.096	5.820
26	EtOH	200	25	1.659	0.095	5.800
27	EtOH	200	20	1.625	0.093	5.659
28	EtOH	200	20	1.554	0.089	5.406
29	EtOH	200	20	1.664	0.095	5.804
30	EtOH	200	20	1.691	0.097	5.885
31	EtOH	200	15	1.586	0.091	5.554
32	EtOH	200	15	1.545	0.089	5.405
33	EtOH	200	15	1.553	0.089	5.365
34	EtOH	200	10	1.549	0.089	5.373
35	EtOH	200	10	1.528	0.088	5.321
36	EtOH	200	10	1.452	0.083	5.078
37	EtOH	200	5	1.372	0.079	4.786

Table B.1 Raw data of the extracted lignin absorbance, concentration, and % yield (Cont.)

No.	Solvent	Power (W)	Time (min)	Absorbance at 280 nm.	Concentration (g/100ml solution)	% Yield
38	EtOH	200	5	1.260	0.072	4.588
39	EtOH	200	5	1.319	0.076	4.610
40	IPA	100	30	0.309	0.018	1.117
41	IPA	100	30	0.276	0.016	0.981
42	IPA	100	30	0.282	0.016	1.003
43	IPA	100	25	0.256	0.015	0.905
44	IPA	100	25	0.250	0.014	0.887
45	IPA	100	25	0.252	0.014	0.894
46	IPA	100	20	0.220	0.013	0.774
47	IPA	100	20	0.192	0.011	0.681
48	IPA	100	20	0.205	0.012	0.725
49	IPA	100	15	0.181	0.010	0.639
50	IPA	100	15	0.212	0.012	0.752
51	IPA	100	15	0.197	0.011	0.696
52	IPA	100	10	0.177	0.010	0.626
53	IPA	100	10	0.160	0.009	0.567
54	IPA	100	10	0.165	0.009	0.585
55	IPA	100	5	0.063	0.004	0.222
56	IPA	100	5	0.064	0.004	0.225
57	IPA	100	5	0.063	0.004	0.223
58	IPA	200	30	0.789	0.045	2.805
59	IPA	200	30	0.747	0.043	2.646
60	IPA	200	30	0.755	0.043	2.681
61	IPA	200	25	0.682	0.039	2.405
62	IPA	200	25	0.655	0.038	2.304
63	IPA	200	25	0.668	0.038	2.365
64	IPA	200	20	0.600	0.034	2.196
65	IPA	200	20	0.524	0.030	1.877
66	IPA	200	20	0.565	0.032	2.007
67	IPA	200	15	0.438	0.025	1.562
68	IPA	200	15	0.499	0.029	1.776
69	IPA	200	15	0.461	0.026	1.638
70	IPA	200	10	0.333	0.019	1.186
71	IPA	200	10	0.317	0.018	1.125
72	IPA	200	10	0.320	0.018	1.133
73	IPA	200	5	0.197	0.011	0.699
74	IPA	200	5	0.209	0.012	0.786
75	IPA	200	5	0.208	0.012	0.737

Standard curve

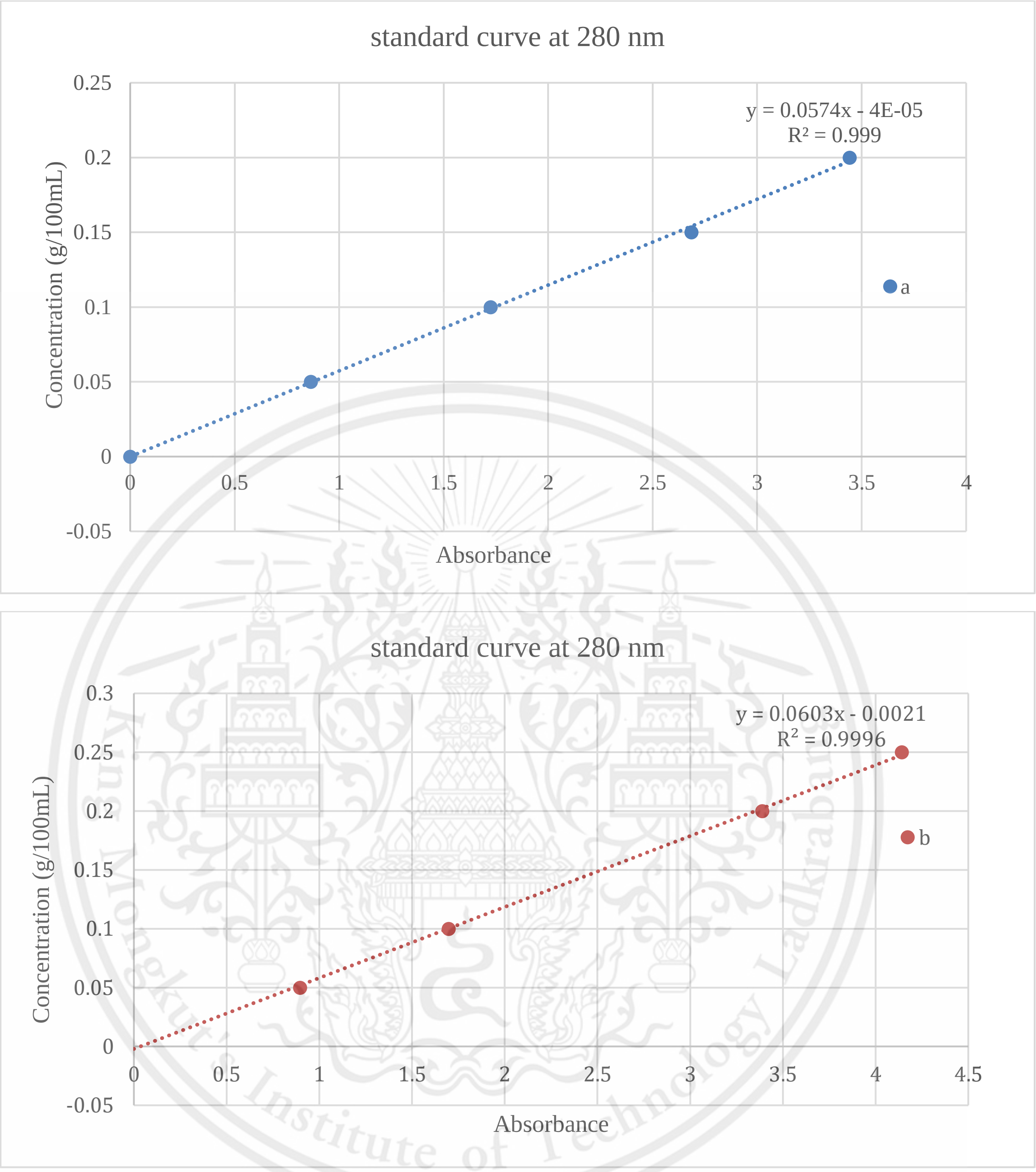

Figure B.1 Standard curves at 280 nm a) standard curve for lignin extracted by using ethanol b) standard curve for lignin extracted by using isopropanol

Lignin concentration was calculated by using standard curve linear line in Figure B.1. Variable x is the measurable absorbance. After that, the variable y is calculated to get lignin concentration.

Appendix C Raw data of % mass loss in the process

Raw data of % mass loss in the process

Table C.1 Raw data of % mass loss in the process

No.	Solvent	Power (W)	Time (min)	$\%M_{loss,O}$	$\%M_{loss,E}$	$\%M_{loss,F}$	$\%M_{loss,S}$
1	EtOH	100	30	1.195	2.878	11.385	7.584
2	EtOH	100	30	1.270	3.755	11.176	8.291
3	EtOH	100	30	0.563	4.593	10.276	9.096
4	EtOH	100	25	1.145	3.016	10.719	7.304
5	EtOH	100	25	0.636	2.727	10.655	7.145
6	EtOH	100	25	1.052	3.502	9.472	7.186
7	EtOH	100	20	0.907	4.226	11.119	8.253
8	EtOH	100	20	1.013	3.999	13.771	6.768
9	EtOH	100	20	0.890	3.397	10.209	8.047
10	EtOH	100	15	0.797	3.153	9.857	7.900
11	EtOH	100	15	1.051	3.532	13.838	6.792
12	EtOH	100	15	1.072	3.507	8.485	8.249
13	EtOH	100	10	0.841	3.685	11.306	7.531
14	EtOH	100	10	0.901	7.026	13.781	7.566
15	EtOH	100	10	1.132	4.602	11.307	5.914
16	EtOH	100	5	0.273	3.743	10.049	6.324
17	EtOH	100	5	0.291	4.127	9.164	7.400
18	EtOH	100	5	2.122	3.247	6.947	6.584
19	EtOH	200	30	1.287	4.242	9.24	7.360
20	EtOH	200	30	1.326	3.525	9.030	8.158
21	EtOH	200	30	1.560	3.302	8.055	7.819
22	EtOH	200	30	1.291	3.582	7.200	8.309
23	EtOH	200	25	1.345	2.345	9.453	7.635
24	EtOH	200	25	1.254	4.725	8.777	8.523
25	EtOH	200	25	1.290	3.233	9.373	7.230
26	EtOH	200	25	1.338	2.820	7.630	8.371
27	EtOH	200	20	1.361	3.557	8.692	7.784
28	EtOH	200	20	1.144	2.724	8.227	8.028
29	EtOH	200	20	1.178	3.189	9.585	7.356
30	EtOH	200	20	1.198	2.015	7.988	7.771
31	EtOH	200	15	1.282	2.221	8.558	7.312
32	EtOH	200	15	1.265	2.638	8.601	7.517
33	EtOH	200	15	1.199	2.471	8.158	7.958
34	EtOH	200	10	1.181	2.981	4.962	8.106
35	EtOH	200	10	1.107	2.069	8.002	8.093
36	EtOH	200	10	1.096	2.066	8.390	7.204
37	EtOH	200	5	1.250	2.283	9.022	7.083
38	EtOH	200	5	1.113	2.156	8.171	7.997
39	EtOH	200	5	1.243	2.486	8.682	7.349

Table C.1 Raw data of % mass loss calculated in the process (Cont.)

No.	Solvent	Power (W)	Time (min)	$\%M_{loss,O}$	$\%M_{loss,E}$	$\%M_{loss,F}$	$\%M_{loss,S}$
40	IPA	100	30	1.164	2.575	7.426	6.668
41	IPA	100	30	1.226	1.694	7.228	6.291
42	IPA	100	30	1.206	2.250	7.219	6.859
43	IPA	100	25	1.016	1.796	5.641	7.618
44	IPA	100	25	1.283	2.983	5.929	7.068
45	IPA	100	25	1.141	2.898	5.923	7.426
46	IPA	100	20	1.144	2.523	8.259	5.718
47	IPA	100	20	1.250	1.666	3.912	8.819
48	IPA	100	20	1.143	1.832	6.604	6.332
49	IPA	100	15	0.960	2.083	6.522	6.757
50	IPA	100	15	1.177	1.937	6.536	6.319
51	IPA	100	15	1.159	1.920	6.412	6.557
52	IPA	100	10	0.781	2.361	8.173	5.975
53	IPA	100	10	0.795	2.566	6.885	6.126
54	IPA	100	10	0.815	2.190	5.757	7.060
55	IPA	100	5	0.344	2.569	7.236	6.132
56	IPA	100	5	0.361	2.923	8.102	5.485
57	IPA	100	5	0.379	3.126	7.788	5.511
58	IPA	200	30	2.862	3.013	8.587	5.333
59	IPA	200	30	2.593	4.584	9.710	6.333
60	IPA	200	30	2.624	4.193	8.718	6.365
61	IPA	200	25	2.717	2.505	8.572	5.343
62	IPA	200	25	2.508	4.140	9.489	6.346
63	IPA	200	25	2.625	2.384	8.721	5.371
64	IPA	200	20	2.429	3.424	9.745	4.770
65	IPA	200	20	2.663	2.962	10.024	5.326
66	IPA	200	20	2.683	2.924	9.406	5.276
67	IPA	200	15	2.496	2.857	9.594	5.383
68	IPA	200	15	2.499	3.011	9.214	4.727
69	IPA	200	15	2.615	2.885	9.588	4.839
70	IPA	200	10	2.396	3.624	9.464	5.181
71	IPA	200	10	2.351	2.863	9.011	5.003
72	IPA	200	10	2.299	2.541	8.681	5.142
73	IPA	200	5	2.556	2.406	9.293	4.872
74	IPA	200	5	2.255	4.282	9.563	5.253
75	IPA	200	5	2.233	2.987	9.113	5.250

Calculated equations

This process was calculated losing mass in each step by Equation C-1

$$M_{EtOH,in}+M_{Wood,in}=M_{loss,O}+M_{loss,F}+M_{loss,S}+M_{loss,E}+M_{solid}+M_{Solution} \quad \text{(C-1)}$$

where

$M_{EtOH,in}$ = initial mass of ethanol

$M_{Wood,in}$ = initial mass of wood

$M_{loss,O}$ = mass loss in extraction process

$M_{loss,F}$ = mass loss in filtration process

$M_{loss,S}$ = mass loss in drying solid fraction

$M_{loss,E}$ = mass loss in process reaction

M_{Solid} = mass of dry solid fraction.

$M_{Solution}$ = mass of solution.

Percentage of mass loss in extraction process was calculated by Equation C-2

$$\frac{M_{loss,O}}{M_{EtOH,in}+M_{Wood,in}}\cdot 100\% = \%M_{loss,O} \quad \text{(C-2)}$$

where

$M_{EtOH,in}$ = initial mass of ethanol

$M_{Wood,in}$ = initial mass of wood

$M_{loss,O}$ = mass loss in extraction process

$\%M_{loss,O}$ = percent mass loss in extraction process

Percentage of mass loss in Filtration process was calculated by Equation C-3

$$\frac{M_{loss,F}}{M_{EtOH,in}+M_{Wood,in}}\cdot 100\% = \%M_{loss.F} \quad \text{(C-3)}$$

where

$M_{EtOH,in}$ = initial mass of ethanol

$M_{Wood,in}$ = initial mass of wood

$M_{loss,F}$ = mass loss in filtration process

$\%M_{loss,F}$ = percent mass loss in filtration process

Percentage of mass loss in drying process was calculated by Equation C-4

$$\frac{M_{Solid,Wet} - M_{Solid}}{M_{EtOH,in} + M_{Wood,in}} \cdot 100\% = \%M_{loss,S} \qquad \text{(C-4)}$$

where

$M_{EtOH,in}$ = initial mass of ethanol

$M_{Wood,in}$ = initial mass of wood

$\%M_{loss,S}$ = percentage of mass loss in drying solid fraction process

$M_{Solid,Wet}$ = mass of wet solid fraction

M_{Solid} = mass of dry solid fraction

Percentage of mass struct in reaction process was calculated by Equation C-5

$$\frac{M_{loss,E}}{M_{EtOH,in} + M_{Wood,in}} \cdot 100\% = \%M_{loss,E} \qquad \text{(C-5)}$$

where

$M_{EtOH,in}$ = initial mass of ethanol

$M_{Wood,in}$ = initial mass of wood

$M_{loss,E}$ = mass loss in reaction process

$\%M_{loss,E}$ = percentage of mass loss in reaction process

Appendix D Raw data of mass of the Klason lignin of the dried wood

Raw data of mass of the Klason lignin of the dried wood

Table D.1 Raw data of mass of the Klason lignin of the dried wood

No.	Lignin weight (g of lignin/g of wood)
1	0.2082
2	0.2046
Average	0.2064

Appendix E Raw data of higher heating value of extracted lignin

Raw data of higher heating value of extracted lignin

Table E.1 Raw data of higher heating value of extracted lignin

Sample name	Higher heating value (cal/g)		
	No.1	No.2	Average
Ethanol+lignin[a]	6179.0	6012.5	6095.8
IPA+lignin[b]	7264.7	7376.3	7320.5

a Ethanol+lignin is the lignin extracted by ethanol extraction with microwave assisted at microwave power 200 W for 30 minutes.

b IPA+lignin is the lignin extracted by isopropanol extraction with microwave assisted at microwave power 200 W for 30 minutes.

BIBLIOGRAPHY

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