Characteristics of Lignin Aerogel from OPEFB Black Liquor of Kraft Pulping Process

Sidthipong Sathawong

A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Environmental Management
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This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgement has been made of any assistance received.

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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์ คุณลักษณะของลิกนินแอโรเจลจากแบลคก์ลิกเคอร์ของทะลายปาล์มเปล่าในการผลิตเยื่อด้วยกระบวนการคราฟท์

ผู้เขียน นายสิทธิพงศ์ สาธะวงค์

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บทคัดย่อ

ลิกนินสามารถนำมาใช้เป็นวัตถุดิบสำหรับการผลิตไฮโดรเจลและแอโรเจล งานวิจัยนี้เป็นการศึกษาวิธีการนำลิกนินที่ได้จากน้ำเสียของกระบวนการผลิตเยื่อคราฟท์จากทะลายปาล์มเปล่าโดยในการทดลองได้ดำเนินการตรวจสอบประสิทธิภาพการแยกลิกนินออกจากน้ำดำเพื่อนำไปผลิตเป็นกัม-ลิกนินไฮโดรเจลและแอโรเจลอีกทั้งยังมีการศึกษาคุณสมบัติของไฮโดรเจลและแอโรเจลซึ่งมีลิกนินเป็นองค์ประกอบ

การหาสภาวะที่เหมาะสมของกระบวนการผลิตเยื่อด้วยวิธีการคราฟท์สามารถทำได้โดยโดยออกแบบการทดลองด้วยวิธีบ็อกซ์และเบห์นเคน (box and behnken design) เพื่อประเมินคุณภาพของเยื่อและคุณภาพของลิกนินซึ่งแผ่นเยื่อกระดาษที่ผลิตขึ้นจะต้องผ่านการทดสอบสมบัติทางกล เช่น ดัชนีความต้านทานแรงกดวงแหวน (ring crush index, RCI) ดัชนีความต้านทานแรงดึง (tensile index, TI) และดัชนีความต้านทานแรงดันทะลุ (bursting index, BI) ทั้งนี้สมบัติของเยื่อกระดาษที่ผลิตได้จากกระบวนการคราฟท์จะถูกนำมาเปรียบเทียบกับเยื่อกระดาษที่ผลิตจากกระบวนการโซดา ผลการทดลองแสดงให้เห็นว่าสมบัติทางกลของแผ่นเยื่อกระดาษที่ได้จากกระบวนการคราฟท์ดีกว่าแผ่นเยื่อกระดาษที่ได้จากกระบวนการโซดาซึ่งแผ่นเยื่อกระดาษที่ได้จากกระบวนการคราฟท์มีค่า RCI, TI และ BI เท่ากับ 0.26 Nm/g, 6.58 Nm/g และ 1.43 kPa.m^2/g ตามลำดับ ขณะที่แผ่นเยื่อกระดาษที่ได้จากกระบวนการโซดามีค่า RCI, TI และ BI เท่ากับ 0.16 Nm/g, 2.74 Nm/g และ 0.65 kPa.m^2/g ตามลำดับ

กระบวนการคราฟท์เป็นวิธีการหนึ่งที่นิยมนำมาใช้ในการกำจัดลิกนินออกสำหรับกระบวนการผลิตเยื่อกระดาษซึ่งลิกนินปริมาณที่ละลายปนเปื้อนอยู่ในน้ำดำจัดเป็นของเสียที่ไม่พึงประสงค์สำหรับกระบวนการผลิตเยื่อ ปกติลิกนินสามารถตกตะกอนแยกออกจากน้ำดำได้ด้วยกรด ดังนั้นจึงทดลองปรับค่าความเป็นกรด-ด่างของน้ำดำให้มีค่าเท่ากับ 2, 3 และ 4 เพื่อหาสภาวะที่เหมาะสมในการตกตะกอน

แยกลิกนิน ผลการทดลองแสดงให้เห็นว่า คราฟท์ลิกนินของทะลายปาล์มเปล่าจะแยกออกจากน้ำดำได้มากที่สุดเมื่อปรับค่าความเป็นกรด-ด่างเท่ากับ 3 โดยจะมีผลผลิตและความบริสุทธิ์ของลิกนินมากที่สุด คือ ร้อยละ 26.02 และร้อยละ 90.35 ตามลำดับ นอกจากนี้ความเป็นกรดยังมีผลต่อการลดลงของค่า COD ในน้ำเสียที่มีน้ำดำผสมปนอยู่ โดยพบว่า ค่า COD จะลดลงมากถึงร้อยละ 38 ที่ความเป็นกรด-ด่างเท่ากับ 2 อีกทั้งยังช่วยลดความเข้มสีของน้ำเสียหลังจากตกตะกอนแยกลิกนินออกแล้ว

คุณสมบัติของลิกนินที่ตกตะกอนแยกได้จะถูกนำไปประเมินความเป็นไปได้ที่จะนำมาใช้เป็นวัตถุดิบสำหรับการผลิตลิกนิน-อะกาโรสไฮโดรเจล ซึ่งคุณลักษณะของลิกนินจะถูกตรวจสอบด้วยเครื่อง Fourier transform infrared spectrometer (FTIR) ลักษณะการกระจายตัวของลิกนินตามน้ำหนักโมเลกุลจะถูกวิเคราะห์ด้วยเครื่อง gel permeation chromatography (GPC) นอกจากนี้ยังมีการนำเครื่อง thermogravimetric analysis (TGA) และเครื่อง differential scanning calorimetry (DSC) มาใช้ในการวิเคราะห์การเสื่อมสภาพทางความร้อนและอุณหภูมิการเปลี่ยนสถานะจากของแข็งคล้ายแก้วเป็นยืดหยุ่นคล้ายยางของลิกนินที่ตกตะกอนแยกได้ตามลำดับ ซึ่งอุณหภูมิการเปลี่ยนสถานะจากของแข็งคล้ายแก้วเป็นยืดหย่นคล้ายยาง (Tg) ของคราฟท์ลิกนินที่ตกตะกอนที่พีเอช 3 มีค่าสูงที่สุด คือ 131.81 องศาเซลเซียส มีน้ำหนักโมเลกุลเฉลี่ยโดยน้ำหนัก (M_w) น้ำหนักโมเลกุลเฉลี่ยโดยจำนวนโมเลกุล (M_n) และการกระจายตัวของน้ำหนักโมเลกุล (polydispersity = M_w/M_n) มีค่าเท่ากับ 1,588, 1,082 และ 1.47 ตามลำดับ

ลิกนิน-อะกาโรสไฮโดรเจลสามารถสังเคราะห์ขึ้นได้โดยใช้อีพิคลอโรไฮดริน (epichlorohydrin, ECH) เป็นสารเชื่อมขวางและจากผลของ FTIR แสดงให้เห็นว่า มีการเชื่อมขวางระหว่างลิกนินและอะกาโรสเกิดขึ้นที่ช่วงความยาวคลื่น 3416 และ 3353 cm^{-1} โดยหมู่ฟังก์ชั่นอะซีทอล (acetal) จะปรากฏที่ช่วงความยาวคลื่น 1179-1178 cm^{-1} ของลิกนินไฮโดรเจล ความแข็งแรงของลิกนิน-อะกาโรสไฮโดรเจลสามารถทดสอบด้วยการวิเคราะห์เนื้อสัมผัส (texture personal analysis, TPA) ซึ่งค่าความเค้นของการแตกหักจะมีความสัมพันธ์กับความแน่นเนื้อหรือค่าความแข็งของไฮโดรเจลทั้งนี้ขึ้นอยู่กับความเข้มข้นขององค์ประกอบภายในไฮโดรเจล จากผลการทดลองแสดงให้เห็นว่า ความแข็งแรงของเจลจะเพิ่มขึ้นเมื่อเพิ่มปริมาณลิกนินและอีพิคลอโรไฮดรินซึ่งสภาวะการทดลองที่มีปริมาณลิกนินร้อยละ 5 อะกาโรสร้อยละ 5 และอีพิคลอโรไฮดริน 10 มิลลิลิตรจะทำให้ไฮโดรเจลมีคุณสมบัติเชิงกลดีที่สุด

ลิกนิน-แซนแทนกัมไฮโดรเจลสามารถเตรียมได้ด้วยการใช้สารเชื่อมขวางเป็นอีพิคลอโรไฮดริน (epichlorohydrin, ECH) ลักษณะพันธะระหว่างคาร์บอนกับคลอไรด์ (ช่วงความยาวคลื่น 740 cm^{-1}) จะไม่ปรากฏอยู่ในตัวอย่างลิกนิน-แซนแทนไฮโดรเจลแต่จะปรากฏสเปกตรัมของพันธะนี้ในตัวอย่างลิกนิน-

แซนแทนไฮโดรเจลที่มีอีพิคลอโรไฮดรินเป็นสารเชื่อมขวางซึ่งเป็นคุณลักษณะเฉพาะของตัวอย่างลิกนินแซนแทนไฮโดรเจลมีอีพิคลอโรไฮดรินเป็นองค์ประกอบ ทั้งนี้ความเข้มข้นของหมู่อะซิทอล (พันธะระหว่างคาร์บอนกับออกซิเจนที่ความยาวคลื่น 1193 cm^{-1}) ในไฮโดรเจลที่มีสารเชื่อมขวางจะเป็นปัจจัยหลักที่ส่งผลกระทบต่อปฏิกิริยาเคมีของหมู่ไฮดรอกซิลในแซนแทนกัมซึ่งมีการเติมสารเชื่อมขวาง

แอโรเจลซึ่งมีส่วนประกอบของลิกนินสามารถเตรียมได้ด้วยกระบวนการที่แตกต่างกันทั้งกระบวนการทำแห้งแบบแช่เยือกแข็ง (freeze drying) และการทำแห้งแบบวิกฤตยิ่งยวด (supercritical drying) ตัวอย่างแอโรเจลที่เตรียมจาก A5L5E10-CPD ซึ่งผ่านกระบวนการทำแห้งแบบวิกฤตยิ่งยวดจะมีพื้นที่ผิวมากที่สุด คือ 2.43 m^2/g และมีความหนาแน่นต่ำโดยจะมีขนาดรูพรุนเฉลี่ยเท่ากับ 16.49 อังสตรอม (1.65 นาโนเมตร) อย่างไรก็ตามตัวอย่างแอโรเจลที่ได้จากกระบวนการทำแห้งแบบแช่เยือกแข็งก็ยังคงให้โครงสร้างที่มีรูพรุนในระดับนาโนเมตรและมีพื้นที่ผิวสูงเช่นเดียวกัน

สุดท้ายนี้เมื่อนำแอโรเจลมาวิเคราะห์จุดอ่อนและจุดแข็งพบว่า จุดอ่อนที่สำคัญของผลิตภัณฑ์แอโรเจลนี้ คือ วัสดุหลักที่ใช้สำหรับการเตรียมแอโรเจลมีราคาสูงโดยเฉพาะอะกาโรส แต่จุดแข็งอย่างหนึ่งที่น่าสนใจ คือ มูลค่าเพิ่มของวัสดุเศษเหลือจากอุตสาหกรรมน้ำมันปาล์มและอุตสาหกรรมเยื่อกระดาษ อีกทั้งมีความเป็นไปได้ในการนำเอาแอโรเจลที่ได้จากงานวิจัยนี้ไปพัฒนาเพื่อใช้ในงานด้านวิศวกรรมการแพทย์และอุตสาหกรรมยาในอนาคต

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Major Program Environmental Management
Academic Year 2017

ABSTRACT

Lignin has been potentially used as a raw material to produce lignin based hydrogel and aerogel products. This research reported the procedure to recover and evaluate the lignin obtained from kraft black liquor of oil palm empty fruit bunches. The experimental analyses were conducted to validate the efficiency of isolated lignin, which was received from a kraft-based dissolving pulp production, to produce the lignin-gum hydrogel and aerogel process. The study also described the properties of lignin based hydrogel and aerogel.

The optimum condition of the kraft pulping process was explored by the Box and Behnken Design to evaluate the quality of pulp and lignin separation. The mechanical properties of pulp sheets were investigated, including the ring crush index (RCI), tensile index (TI), and bursting index (BI). The quality of kraft pulp was compared to the soda pulp. It was found that the mechanical properties of pulp sheets obtained from the kraft pulp are better than that of pulp sheets obtained from the soda pulp. The pulp sheets from kraft pulping process contributed the higher RCI, TI, and BI which were 0.26 Nm/g, 6.58 Nm/g, and 1.43 kPa.m^2/g, respectively. On the other hand, the soda pulp sheets had the RCI, TI, and BI of 0.16 Nm/g, 2.74 Nm/g, and 0.65 kPa.m^2/g, respectively.

Kraft process is one of the most frequently used methods for the delignification of wood pulping. The large quantities of lignin in black liquor are the unwanted by-product of pulping waste. Normally, the lignin can be precipitated from black liquor by the acidic method. Lignin from the OPEFBs black liquor was precipitated at pH 2, 3 and 4 to determine the optimal condition of lignin separation. The results showed that the isolated lignin from the kraft black liquor of OPEFBs was greater intensity at pH 3. It contributed the highest yield and purity of lignin as 26.02% and 90.35%, respectively. Moreover, acidic pH has effected on the decreasing of chemical oxygen demand (COD) for wastewater with black liquor content. COD reduction was up to 38% at pH 2 and also showed a tendency to decrease the color of wastewater after lignin separation.

The properties of isolated lignin were evaluated to consider the possibility of their use as the raw material of lignin-agarose hydrogel. Lignin characteristics have been performed using Fourier transform infrared spectroscopy (FT-IR). The molecular weight distribution of isolated lignin was determined using gel permeation chromatography (GPC). The thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) were used to determine the thermal degradation and the glass transition temperature, respectively. The glass transition temperature (T_g) values of the kraft lignin precipitation at pH 3.0 was the highest (131.81°C). The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (polydispersity = M_w/M_n) of the kraft lignin precipitated at pH 3.0 were 1588, 1082, and 1.47, respectively.

Lignin-agarose hydrogel was synthesized by using epichlorohydrin as the cross-linking agent. FTIR recognized that the crosslinking between lignin and agarose has happened at the bands of 3416 and 3353 cm^{-1}. The vibration peaks of the acetal, 1179-1178 cm^{-1}, was occurred in the lignin-based hydrogel. Gel strength of lignin-agarose hydrogel was characterized by texture personal analysis (TPA). The results demonstrated that the gel strength increased with increasing of lignin and ECH in agarose solutions. 5% lignin, 5% agarose and 10 ml ECH contributed the best gel formation and the excellent mechanical properties.

Lignin-xanthan gum hydrogel was prepared by chemical crosslinking of epichlorohydrin (ECH). The characteristic peaks of the C–Cl bond (740 cm^{-1}) are not present in the XL hydrogel but appear in the FT-IR spectrum of the XL-ECH hydrogel. This is the characteristic of the XL-ECH hydrogel samples. The intensities of the acetal, C–O peak at 1193 cm^{-1}, in XL-ECH hydrogel were the main factor that impact on the chemical reaction of –OH group in xanthan gum which had a presence of a crosslinking agent.

Lignin based aerogels can be prepared in the different processes including freeze drying and supercritical drying process. The A5L5E10-CPD aerogel obtained from supercritical drying process has the high surface area of 2.43 m^2/g with the low density, which has the average pore sizes of 16.49 Å (1.65 nm). However, the aerogel from freeze drying contributed a nanoporous structure and minimize surface area.

Finally, the strengths and weaknesses of lignin based aerogel were analyzed. It was found that the important weaknesses of lignin based aerogel is the higher cost of material used to prepare the aerogel, especially agarose. At the same time, the strength of lignin based aerogel is value-added of residual materials from the palm oil industry and the pulp and paper industry. It is also possible to use the aerogels in this research to further develop in the field of medical engineering and pharmaceutical industries in the future.

ACKNOWLEDGEMENT

First of all I would like to thank my advisor and co-advisor, Assoc. Prof. Dr. Waranyou Sridach and Asst. Prof. Dr. Kua-anan Techato for the great support and advice to my Ph.D. studying and writing thesis. For the examining chairperson and committee, I would like to express my gratitude to Asst. Prof. Dr. Pratuang Puthson, Asst. Prof. Dr. Wirach Taweepredaa and Asst. Prof. Dr. Chaiwat Rongsayamanont for their valuable time and intensive guidance for my thesis. I particularly thank to the Office of Higher Education Commission (OHEC) and Graduate School, Prince of Songkla University for the grant including Yala Rajaphat University (YRU) for their financial and facility support. I am grateful thanks the professors at faculty of Environmental Management Prince of Songkla University for comment. I really acknowledge the education officers in faculty of Environmental Management Prince of Songkla University to support and coordination for everything. I really thank the department of Material Product Technology at faculty of Agro-Industry Prince of Songkla University for greatly support in the experimental location.

Deepest thanks and appreciation to my family and others for their cooperation, encouragement, constructive suggestion and full of support for the dissertation completion, from the beginning till the end. Also, thanks to all of my cliques and everyone, those have been contributed by supporting my work and help me during the Ph.D. Program till completed.

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CHAPTER 1

INTRODUCTION

1.1 Background and rational

Oil palm is one of the major industrial crops of the southern locale of Thailand. The unrefined palm oil industries assume a critical part in the financial improvement of the nation and in upgrading the commercial welfare of the population (Chavalparit *et al*., 2006). Many organizations are dealing with crude palm oil extraction and purification to produce oil palm for utilization. The oil palm plantations expanded to 1.8×10^2 acres and the collecting of fresh fruit bunches come to around 7.5×10^2 tons in 2009 (Phitthayaphinant and Nissapa, 2010). Palm oil production produces a lot of solid residues including shells, cellulosic fibers and oil palm empty fruit bunches (OPEFB). The fresh fruit bunches were cleansed with steam during the extraction processes. It is the reason for the high moisture content in oil palm empty fruit bunch residues which make them unsatisfactory as a fuel. In addition, they introduce the great troubles in disposal and useless in terms of cost. (Chavalparit *et al*., 2006).

At present, OPEFB solid wastes have turned into a major trouble of elimination in the oil palm industry. In any case, the previous research demonstrates that OPEFB fiber is made up from a complex matrix of three principle polymers which are cellulose, hemicellulose and lignin. It constituted approximately around 43.2% cellulose, 32.5% hemicellulose and 26.2% of the lignin (Jeffries, 1994; Astimar *et al*., 2002; Boerjan *et al*., 2003; Rosli *et al*., 2004). It also reported that OPEFB is composed 31.9% glucan, 21.4% xylan and

1.5% arabinan (Ming *et al.*, 2010), while the non-structural constituents mainly refer to ash and extractives accounted for 0.10% and 11.87%, respectively. (Rosli *et al.*, 2004).

Pulp and paper manufacture is one of the popular demand divisions in the world of industrial manufacture. The total global consumption of paper and paper board was anticipated from 361×10^6 tons in 2005 to achieve 510×10^6 tons by 2020 (Gracía *et al.*, 2008). Innovation pulp and paper has beaten the greater part of the related ecological issues. Recent raw materials have supplanted conventional wood raw materials with non-wood and residual materials. The less polluting cooking and pulp bleaching forms have been developed. The ecological issues have delivered the cleaner innovation engaged in paper making.

Cleaner innovation is connected to accomplish the expanded generation with least impact on the environment, and to save, utilize, and reuse costly and rare chemicals and raw materials. This innovation is additionally called low and non-waste technology (Müller, 1986). The innovation decreases the transfer costs, stability risks, asset costs brings about a diminished weight on the environment and increase excesses. A new innovation is fundamental for a clean industry, whereas this choice is to a great extent because of the costs of the innovation required.

Pulping is the process by which wood is reduced to a fibrous mass that for breaking the bond inside the wood structure. The commercial procedures are normally categorized as mechanical, semimechanical or chemical pulping.

The chemical pulping is utilized on paper making delivered economically in the world. Generally, it has included a full chemical treatment in which the goal is to extract the noncellulose wood parts leaving in place the cellulose fibers. By and by, detachment of the components have been never totally perceived. However acceptable bargains become to the procedures which yields close to 40 - 60% of the wood mass. Two main methods of chemical pulping process are the acidic process, such as sulfite process (Figure 1.1) and the alkaline process, such as kraft process (Figure 1.2).

The kraft process is the most commanding chemical pulping process. The expression of “sulfate” is gotten from the constitution sodium sulfate. The kraft process includes the recuperation around to constitution for chemical lost. The active cooking chemicals of kraft pulping process are sodium sulfide (Na_2S) and sodium hydroxide ($NaOH$). The kraft pulp contributed the better pulp quality in contrast to sulphite pulp. The kraft pulping process delivered an assortment of pulps utilized principally to package and high-quality papers and paperboard. It has affected to the environmental controls on outflows from industry, for example, add up eliminated solids, sulfur compound, sulfur dioxide, and wastewater contamination.

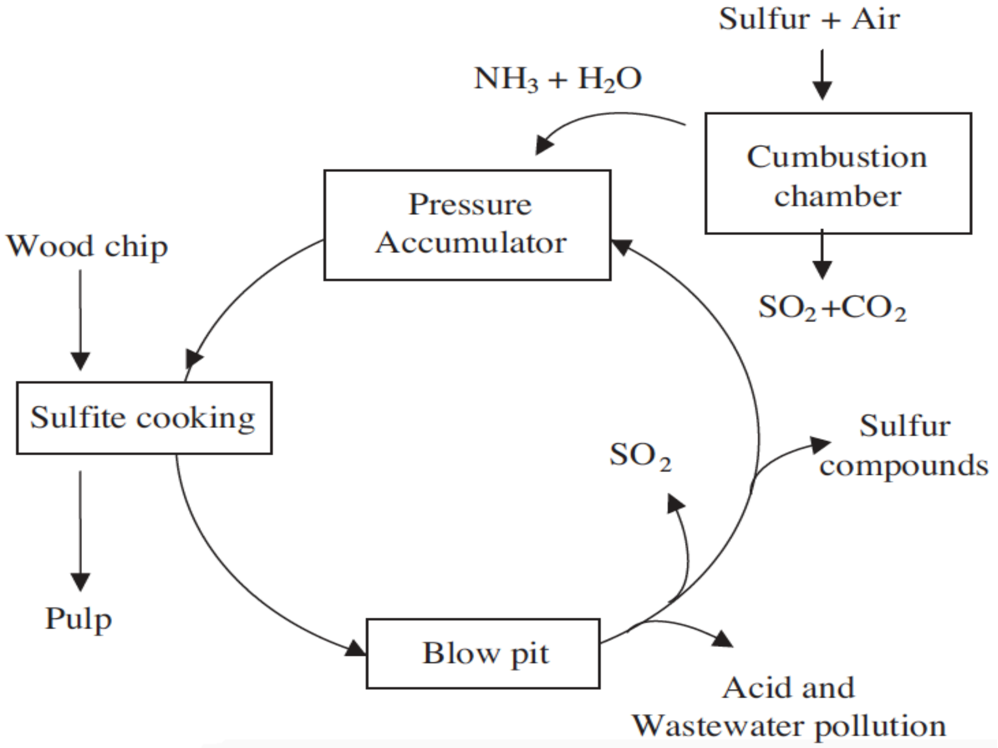


Figure 1.1 Sulfite process (Sridach, 2010)

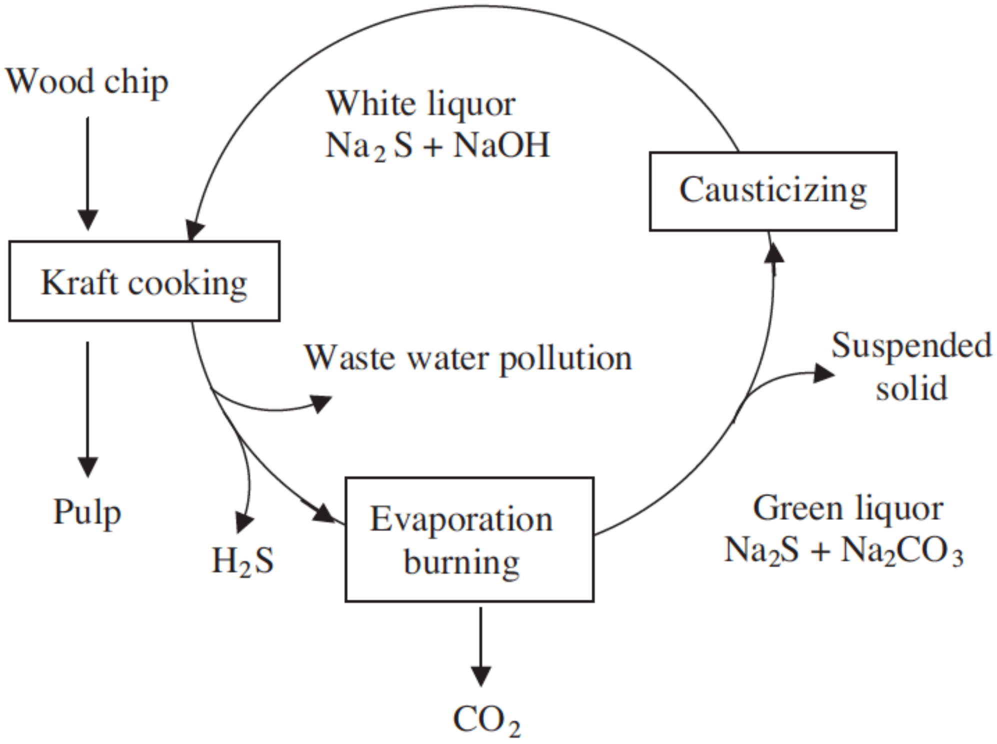


Figure 1.2 Kraft process (Sridach, 2010)

Any type of wood can be pulped basically by the kraft procedure since it produces the strongest pulps with the greatest financial aspects. Hence it has become the predominant procedure in the world. Nevertheless, the output of pulp in current annual does not meet the strong growth in demands, which are growing excellently and continuing in developed countries. Therefore, it is leading to an enlarging shortage of wood raw materials and a slow deforestation of some area in the planet.

Many researches have been studied and looked for a new, non-wood raw material for paper production. It has been conducted in Europe and North America (Anttila *et al*. 2012; Karjalainen *et al*. 2013; Le Normand *et al*. 2012). The cellulose fibers about 60% originate in developing country from non-wood materials such as bagasse (sugarcane fibers), cereal straw, bamboo, reeds, and OPEFB.

Black Liquor is a very dark wastewater resulting from pulping process of pulp and paper industries. It’s made out of dissolvable and colloidal organic and inorganic components coming from the digestion of wood and extracted in the aqueous media from the cellulose fibers amid the washing process. The chemical components of black liquor are corrupted lignin, extractable soap or tall oil, hemicellulose and hydroxyl acid, and numerous types of inorganic such as NaOH, Na_2CO_3, Na_2SO_4, Na_2S, and small amounts of Ca, Mg, Si, etc. Its compounds depend on type, age, and seasoning of wood feedstock, including the digestion and washing process (Alén *et al.*, 2003; Wallberg *et al.*, 2003; Domenek *et al.*, 2013). Therefore, the composition of black liquor can fluctuate impressively. The black liquor is burned in order to recycle these chemicals and contribute the production of energy for next pulping. Then lignin in black liquor is also burned to get energy. However, this lignin have been separated from black liquor to be applied in many fields for examples dispersant (Estellé *et al.*, 2013), coating (Chotinantasaeth, 2007), vanillin synthesis (Fache *et al.*, 2015) and lignosulfonate synthesis (Domenek *et al.*, 2013).

Lignin is a three-dimensional polyphonic macromolecule of extremely complex structure and it is one of the major components in plants. It comprises of numerous subunits combined with both C-O-C and C-C linkages. The function of lignin in nature is to give inflexibility and union to the cell dividers of materials, to give waterproof to xylem vessels, and to shape a physicochemical fence antimicrobial assault (Mussatto *et al.*, 2007). Generally, lignin is a waste product from the pulp and paper industry, and is frequently utilized as fuel for the energy equilibrium of pulping process (Rosli *et al.*, 2017, Ciolacu *et al.*, 2012). Despite efforts in the past to locate high value-added applications to lignin. For example, it has the small particle size, hydrophobic behavior, and ability to form stable mixtures, which appropriate for the generation of organic aerogel (Grishechko *et al.*, 2013a). Lignin has been demonstrated that lignin glyoxalated can be a powerful substrate of adhesive resin for formaldehydefree particleboards (Çetin *et al.*, 2002). Furthermore, potential health applications of lignin have been investigated (Vinardell *et al.*, 2008).

Organic aerogels are highly porous materials consolidating various incredible and unique characteristics, for example, great lightweight, high surface area and customizable mesoporosity (8 nm < pore width < 80 nm). They have been recommended as thermal insulators (Razzaghi *et al.*, 2015) or drug conveyance materials (Veronovski *et al.*, 2014 and Ciolacu *et al.*, 2012). Moreover, they might be utilized as high surface area adsorbents (Wörmeyer *et al.*, 2014 and Carrasco-Marin *et al.*, 2009) and cathodes for the capacitor after pyrolysis (Szczurek *et al.*, 2010 and Amaral-Labat *et al.*, 2012)

Generally, organic aerogels are made by hydrogel polycondensation which are the response of monomers with aldehydes, particularly phenolic compounds such as resorcinol (Grishechko *et al*, 2013b). Resorcinol–formaldehyde gels are organic aerogels and have been generally explored as a result of their fantastic and reproducible properties. Nonetheless, the high cost of resorcinol never allowed any large-scale manufacturing of resorcinol-formaldehyde gels and motivated scientists to search for new and cheap raw materials, which may prompt comparable materials.

Currently, various phenolic compounds that could be progressively utilized as gel precursors (Mukai *et al.,* 2005) and different sorts of tannin (Szczurek *et al.,* 2011 and Braghiroli *et al.,* 2014) or lignin (Chen and Li, 2010 and Chen *et al.,* 2011).

This research is to produce the kraft lignin from OPEFB and the lignin aerogel product. The kraft lignin of OPEFB was precipitated by using acidic technique. This research has been measured the optimal condition of kraft lignin precipitation. Some chemical and physical properties of OPEFB kraft lignin were investigated. The isolated lignin can be used to produce the lignin based hydrogel. This study established the lignin-gum hydrogel using epichlorohydrin as the cross-linking agent. The appearance and rheology of the composite lignin-gum hydrogel were studied by texture personal analysis (TPA) and viscosity brookfield method. The morphology and functional groups of lignin-gum aerogels were studied by scanning electron microscope (SEM) and the fourier transform infrared spectrophotometry (FTIR).

1.2 Objectives

- To study the optimal condition of kraft pulping for OPEFB's lignin production.
- To study the optimal condition for lignin separation from kraft black liquor by acidifying process.
- To study the optimal conditions of organic hydrogel preparation from the OPEFB's lignin, agarose and xanthan gum.
- To study the effect of drying process on the properties of lignin aerogel.
- To assess the economics of agarose-lignin aerogel production.

1.3 Scope of Work

The black liquor used in this study was from the kraft process of OPEFB which was cooked by using batch reactor. Lignin from black liquor was separated by acidifying process. Then, the organic hydrogels were prepared from OPEFB's lignin and gum (agarose and xanthan). The aim of this study is to investigate chemical reaction between gum-lignin hydrogel including the structural analysis and physical properties of organic aerogel which are produced by different drying process, supercritical and freeze drying. Finally, the economic assessments of commercial aerogel products were investigated.

CHAPTER 2

THEORETICAL CONSIDERATION

2.1 Theoretical Backgrounds

2.1.1 Kraft Pulping Process

There are various methods for producing chemical pulp, but the most utilized process in the world is kraft pulping. The fibers must be freed from each other by removing the lignin. In the process of kraft pulping, this is done at high temperature by adding white liquor (sodium sulfide, Na_2S and sodium hydroxide, NaOH) to the chipped wood. In cooking, dissolvent extracts both lignin and hemicelluloses from cellulose (Brodin, *et al.* 2010).

Kraft pulping involves treating wood chips and sawdust with a sodium hydroxide and sodium sulfide solution. The highly alkaline chemical and wood blend are cooked with steam under pressure for 60-180 minutes. Digestion might be either a nonstop procedure or treated in discontinuous "batches". A large portion of the lignin and a portion of the hemicellulose is dissolved, leaving the rest of cellulosic fibers.

The cooking liquor comprising the dissolved lignin and different extractives (black liquor) is directed to a chemical recovery plant where the lignin and organic wastes are burned to generate energy required in the pulping process. Important extracts (e.g., resin, tall oil, and turpentine) are isolated available to be purchased as item chemicals. Chemicals have been recovered with just a moderately little loss in volume, and after renewal with sodium salts, which come back to the digester for reuse. The brown stock is washed, screened, and gone through the low-density cleaner. These can change generally in the kind of utilized chemicals and their succession. Bleached pulp is then prepared for the paper making process (Gellerstedt and Li, 2001).

Both softwood and hardwoods can be pulped by the kraft process. Amount of fiber recovery depended on the wood species, the temperature of cooking and time, the level of bleaching, and the paper strength. For the most part, kraft pulp retrieves from softwoods are around 45% for unbleached pulp and 40% for bleached pulp. Hardwood recoveries range from 47% to 55% of unbleached pulp to 52% for bleached pulp.

2.1.2 Chemical reaction during kraft pulping process

In cooking, the main goal is to facilitate the deterioration of wood into fibrous product. This is accomplished by softening the bonds in the lignin macromolecule. The principle chemical reactions in the cooking process can be described as (Sjostrom, 1981):

$$NaOH + NaS_2 + Wood \Longrightarrow \text{Na-org.} + \text{S-org.} + NaHS$$

Where the wood presents to a wide range of organic compounds such as lignin, cellulose, hemicellulose, and resins. The hemicellulose can be partitioned into three major organic groups: Glucomannan, Xylan and other hydrocarbon groups.

Chemical compositions of woods:

Cellulose: 35- 44%
Xylan: 5-25%
Glucomannan: 1-23%
Lignin 20-30%
Resins 3-5%
Other hydrocarbons < 4%

Chemical composition of the pulp product:

Cellulose: 70-80%
Xylan: 10-30%
Glucomannan: 2-10%
Lignin 2-5%
Resins: <1%
Other hydrocarbons. <1%

Cellulose is fundamentally a long molecule chains framed by the monomer of glycose. Any reactions of the cellulose molecules are not required to produce pulp.

Consumption of alkali, the solution of sodium sulphite and sodium hydroxide in water is generating equilibrium as follows:

$$S^{2-} + H_2O \Leftarrow\!\!=\!\!\Rightarrow SH^- + OH^-$$

$$SH^- + H_2O \Leftarrow\!\!=\!\!\Rightarrow S_2H + OH^-$$

Alkali in the cooking liquor is basically devoured in three unique reactions: (1) lignin, (2) neutralization of organic acids, and (3) resins in the wood.

(1) Reactions with lignin

In alkaline conditions, the carbon to carbon bonds are stable. The cleavage of oxygen and carbon bonds are the hugest reaction in the cooking process. This reaction will take place and is producing phenolic hydroxyl groups from the fracture of the aryl-alkyl-ether bounds. The phenolic carbons are in the subsequent reaction principally changed over to stilbene (Lachenal *et al*., 2004).

(2) Neutralization of organic acids

The vast majority of the alkaline is expended in the cooking process by the saccharinic acids composed in the degradation of hemicelluloses. The hemicellulose is a polysaccharide substance that incorporates of arabinose, arabinogalactane, arabinoglucoronxylan, glucomannan, glucoronxylan, and glucorans. The saccharinic acids were formed by isosaccharidic acids, formic acid, acetic acid, and milk acid.

(3) The reaction of the resin wood

In the cooking reaction, the sodium salts and harts resins are occurring a soap. They are usually skimmed from the black liquor in the evaporation area. They are additionally handled to deliver tall oil.

2.1.3 Lignin

In the past, lignin was called the chemical substances of wood. After that, it was called only part of noncellulose in wood. In the present, part of noncellulose can be isolated to many types of chemical substances such as carbohydrate, tannins, rosins and lignin etc. Then these chemical substances were investigated widely in many fields.

Normally, lignin is insoluble water, unless it is degraded by physical or chemical treatments. The amount of lignin in the wood varies according to the type of woods. Table 1 shows the amount of lignin in various woods.

Table 2.1 Lignin contents of various woods.

Wood	Lignin content (%)
Noble fir	27.4
Jack pine	24.8
Pinus pine	25.0
Hemlock-spruce	24.8
Montana oak	23.3
Red maple	20.8

Source : Othmer, 1968.

Lignin is the second of most abundant sustainable natural issue on earth, instantly after cellulose. It accompanies in wood and other plant tissues. The amount of lignin in plants varies widely and is normally in range of 16-28% by weight. In admixture with hemicellulose, it shapes the establishing material for cellulose fibrils and imparts strength to the auxiliary components of the plants. In chemical structure, researchers were indistinct about the idea of this extremely plentiful material. It had a higher carbon content when compared to the carbohydrate. Until in 1954 Lange *et al*, who applied UV microscopy at various wavelengths directly on thin wood section, obtained the lignin spectrum. This lignin spectrum indicated typical of aromatic compounds, Thus the chemical structure of lignin was aromatic combination (Sjostrom, 1981). However, it was an amorphous polymer which is complex to discover a true structure.

Beside aromatic structure, other lignin structure also consisted of hydroxyl, methoxyl and carbonyl groups. The differential types of lignin also differ in these functional groups. Therefore, lignin can be nomenclatured with source, such as wheat straw lignin, softwood lignin and hardwood lignin. In a same way, it can be called by extraction method such as native lignin (protolignin), milled wood lignin (MWL), sulfite lignin and kraft lignin, etc (Sjostrom, 1999).

Although lignin was applied in many products, it was used a few percents when compares with million tons of wood. It was due to the cost of lignin production was higher than petrochemical production in the same application. However, the amount of petrochemical materials decrease continuously and being higher cost. Therefore, lignin becomes important material again.

2.1.3.1 General properties of lignin

Lignin is a brown solid powder. Its density and reflective index are 1.3-1.4 g/cm^3 and 1.6, respectively. Normally, it does not dissolve in water and strong mineral acid solution. Sulfuric acid (72%) can separate lignin from other wood carbohydrate. However, lignin are almost dissolved in alkaline solution. A little lignin are soluble in oxygenerated organic compound and amine. X-ray diffraction indicated that lignin was amorphous polymer. In addition, lignin is a branch polymer due to its low specific viscosity. For the energy recovery, lignin contributed the energy of 29.5 MJ/kg for the combustion (Othmer, 1968).

2.1.3.2 Component and structure

Chemical component of lignin was shown in Table 2

Table 2.2 Chemical components of lignin in wood.

Species	%C	%H	%O	%OCH_3
Coniferous	63.8	6.3	29.9	15.8
Deciduous	59.8	6.4	33.7	21.4

Source : Othmer, 1968.

Lignin is a phenolic polymer, which is developed by oxidative coupling of three major C_6-C_3 (phenylpropane) unit, showed in Figure 2.1. The phenolic polymer of lignin comprised of guaiacyl alcohol (G), syringyl alcohol (S), and ρ-hydroxyl alcohol (H). It was formed a randomized structure in a tridimensional network inside the cell wall. The differential lignin had also altered of G, S, H unit composition (Hofrichter *et al.,* 2001).

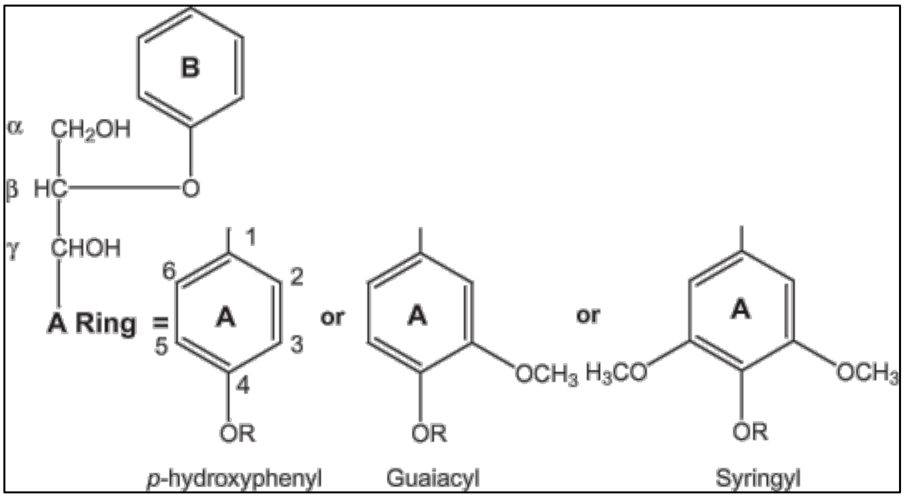


Figure 2.1 Syringyl (S), Guaiacyl (G) and ρ-hydroxyl alcohol (H)

2.1.4 Lignin Recovery

Kraft process are involved in industrial paper, which wood is converted into wood pulp and then into paper. Besides, the process has produced some toxic byproducts such as black liquor. This liquid mixture of pulping residues such as lignin and hemicellulose and inorganic chemicals from the Kraft process such as sodium hydroxide and sodium sulfide have caused of pollution.

Black Liquor is a very dark wastewater resulting from pulping process of pulp and paper industries. It made out of soluble and colloidal organic and inorganic components originating from the digestion of wood and separated in the watery media from the cellulose fibers during the washing process. The chemicals that are the component of black liquor are such as degraded lignin, tall oil, hemicellulose and hydroxyl acid, and numerous species of inorganic. Generally, it is usually dark brown color, higher in BOD, TDS and pH which resulted from alkaline process.

The black liquor is typically 25-30% solids by weight and these so-called "black liquor solids". These solids consisted of lignin in range 24-37 % by solid weight (Alen *et al.,* 2003; Theliander, 2007). The black liquor components are illustrated in Table 3

Table 2.3 The black liquor components.

Element	Weight (%)	Organic material	Weight (%)
Carbon	30-40	Lignin	24-37
Oxygen	31-37	Hydroxy acids	20-33
Sodium	16-27	Extractives	1-4
Hydrogen	2-6	Formic acid	~ 4
Sulphur	3-7	Acetic acid	~ 2
Potassium	0.1-2.2	Methanol	~ 2

Source : Theliander, 2007.

Methods for lignin separation from plants are 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.

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. Moreover, chemical used in the digesting process could 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.

Lignin, which has been increased in its essence in many industries can be derived from plants. In order to use, lignin must 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 a plant, which alters the chemical composition of lignin and makes lignin extremely heterogeneous (Chotinantasaeth, 2007).

2.1.5 Application of Lignin

Lignin can be utilized as a part of many fields because of 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 cement to reduce the amount of water in a concrete to achieve certain smoothness. Furthermore, it enhances the concrete quality. Second is the use of lignin as an additive to animal feed where lignin is used to improve the pellet quality and production efficiency due to its excellent bonding quality. The animal feed-pellets become harder and dust development is reduced. The third is as an additive to duroplasts where lignin is added to aminoplast or phenoplast glues in the production of particle board. Lignin will improve the adhesive properties at low temperatures. Other applications of lignin are, for examples, additives for the composite colors, an additive in crude oil well drilling muds, chemical raw material for the synthesis of vanillin, undergo pyrolysis to form nonionic surfactants for oil recovery (Saake and Lehnen, 2007). Moreover, lignin can be used in the organic aerogel (Grishechko *et al.,* 2013a)

2.1.6 Natural Gum

Natural gums are polysaccharides which equipped for causing a large increment in a solution viscosity, even at little quality. In the food manufacture, they are used as emulsifying agents, and stabilizers. In other productions, they are additionally utilized as adhesive, encapsulating agents and foam stabilizers. Frequently these gums are found in the woody components of plants (Bhardwaj *et al.,* 2007).

Natural gums can be classified according to their origin or as uncharged or ionic polymers (polyelectrolytes). Examples include:

Natural gums obtained from seaweeds:

- Sodium alginate (E401)
- Agar (E406)
- Carrageenan (E407)

Natural gums obtained from non-marine natural assets:

- Locust bean gum (E410), extracted from the seeds of the carob tree
- Guar gum (E412), also called guaran, is a substance made from guar beans
- Gum arabic (E414), from the tree *Acacia* senegal
- Karaya gum (E416) exudate by trees of the genus *Sterculia*
- Tara gum (E417), the endosperm of the seeds of the tara tree

Natural gums produced by bacterial fermentation:

- Xanthan gum (E415), from the bacterial coat of *Xanthomonas campestris*
- Gellan gum (E418), produced by the bacterium *Sphingomonas elodea*

Remark : E number is the food additive code

2.1.7 Agarose

Agarose is a neutral polysaccharide extracted from the cell walls of certain *Rhodophyceae* algae, generally called agarophyte seaweeds. It comprises repeating units of exchanging 3,6-anhydro-α-L- galactopyranosyl and β-D-galactopyranosyl groups (Millán AJ *et al.,* 2002). Its chemical structure enables agarose to form solid gels even at low concentrations. Gels of agarose provide a moist environment and enhance the stability of the system when it is in combination with other polysaccharides. Because of these properties, agarose has been utilized in the preparation of hydrogel scaffolds (Yamada *et al.,* 2012), cartilage (De Rosa *et al.,* 2006), neural tissue (Martin *et al.,* 2008) and wound healing (Lindenbaum *et al.,* 1995).

The physical gelation of such polysaccharides is a complicated procedure of self-get together joined by biomolecular rearrangement and molecular crosslinking (Morris, 2009). Polymer concentrations, the attendance of solutes, temperature history, blending rate, and also dissolvable properties further establish the mechanism of gelation and gel properties. The exact gelation mechanism of agarose is not entirely comprehended. The investigation of kinetic and diffusion processes, as well as concentration flocculation involved in the gelation mechanisms. The gelation process is comprehended regarding liquid-liquid stage.

The mechanical properties introduced by agarose are like those of tissues and can be effectively customized by differing polymer concentration. At the point when dissolved in water, it shapes a gel with arigid arrange, resulting on a three-dimensional porous structure giving a decent environment for cell adhesion, spreading and multiplication. (Cao *et al.*, 2009; Mano *et al.*, 2007; Martin *et al.,* 2008; Trivedi *et al.*, 2014)

Moreover, agarose hydrogels might be polymerized in situ reducing the invasiveness of the surgery and furthermore enable the hydrogel to get the required shape. (Varoni *et al.,* 2012)

2.1.8 Xanthan gum

Xanthan is an exopolysaccharide obtained from the bacterium *Xanthomonas campestris* by aerobic fermentation. It is utilized in the food industry as stabilizing, thickening or suspending agent. Due to its one of a kind rheological properties (high viscosity, an extensive variety of temperature, pH and salt concentration). The xanthan molecules have a (1,4)-β-d-glucopyranose spine as in cellulose, still moreover have a trisaccharide side chain on each other glucose residue linked. The side chain comprises two mannopyranosyl residues connected on either side to a glucuropyranosyl uronic acid group. The spine associated with the inner mannose residue might be acetylated while the terminal mannose residue might be pyruvate. Xanthan particles have the molecular mass very high (more than 3.2×10^{6}) and dissolve in water to extremely viscous solutions (Yawalata *et al*., 2004). The level of pyruvate substitution relies on the aging procedure and the strain of *Xanthomonas* bacteria. In the solid state, xanthan gum is a very symmetric helix adaptation (Rincón *et al.,* 2014).

Xanthan gum has been utilized as a part of a wide assortment of foods (Akdeniz *et al.,* 2006) for various imperative reasons, including emulsion stabilization, temperature stability, and compatibility with food ingredients (Jiangyang *et al.,* 2008). It has turned into one of the most successful hydrocolloids mostly because of its high usefulness, especially in troublesome situations, for example, corrosive, and high shear stress. Its anionic characteristic is due to the presence of both glucuronic acid and pyruvic acid groups in the side chain, hence, offers a potential utility as a bioactive substances transporter as a result of its idleness and biocompatibility (Gils *et al.,* 2009).

2.1.9 Organic Aerogel

In 1931, Samuel Kistler prepared the first organic aerogel by using the jelly made of the natural heteropolysaccharide pectin, who likewise prepared aerogels of gelatin. The expression “organic aerogel” can mention to one of many different types of aerogels. Fundamentally, an organic aerogel is any aerogel with a structure essentially involved natural polymers. Organic aerogels have altogether various properties from inorganic aerogels, such as metal oxide aerogels and silica aerogel. They are normally less friable and fragile than inorganic aerogels. They are rather squishing when compressed. The organic aerogels can be produced using phenol formaldehyde, resorcinol formaldehyde, cresol formaldehyde, melamine formaldehyde, polystyrenes, polyurethanes, agarose, and many others (Ashley *et al.,* 2001).

There are various examples of organic aerogels that have been set up in the literature. Biologists have used supercritical drying to safeguard natural samples or set them up for electron microscopy making aerobacteria and aeroinsects. Organic materials are regularly nanostructured and as often as possible contain water-filled nanoporosity which makes the material to shrink upon dehydration. However, by replacing the water in the pores of the material with ethanol and then replacing the ethanol with liquid carbon dioxide. The sample can be supercritically dried at naturally perfect temperatures deserting a dry.

2.1.10 Applications of Aerogels

Aerogels are promising materials introducing alluring properties because of their high nanostructured porosity, opening a wide field of utilizations:

- High-performance insulation.
- Space: cosmic or cometary dust collection (NASA's Stardust Project).
- Carbon aerogels are electrically conductive: cathodes for batteries and capacitor.
- Encapsulation media.
- Acoustics: sound absorption (anechoic chambers), efficient ultrasonic devices.
- Hydrogen fuel stockpiling.
- Catalysis: Aerogels are for perceived as excellent catalysts and catalyst supports.

2.2 Literatures Review

Narapakdeesakul *et al.,* (2013a) employed to recover and assess the lignin acquired from the black liquor of oil palm empty fruit bunches. The potential utilization of the recovered lignin for the making of linerboard coating was likewise studied. The impact of the pH (2, 3, 4, and 5) of the black liquor on the recovery mass and the qualities of the lignin from the oil palm empty fruit bunches were considered. The recovery mass of lignin enlarges with reducing the pH of the black liquor. The results showed that modifying the pH did not influence the chemical components of the recovered lignin. In any case, the structure of the recovered lignin continuously degraded when a lower pH was applied. Accordingly, to keep away from the over degradation of lignin from acidification, the lignin of the oil palm empty fruit bunches recovered at pH3 was chosen for the planning of linerboard coating.

Narapakdeesakul *et al.* (2013b) synthesized the lignin from the oil palm empty fruit bunches by soda pulping process (20% NaOH solution) was set up at 160 ˚C for 140 min. OPEFB's lignin dissolved in acetone was joined with a blend of palm oil and concentrated sulfuric acid at the ratios of 1:1 and 1:2 (w/w). The mechanical properties of linerboards coated with OPEFB's lignin subsidiary based coatings like those with commercial wax coating. This investigation proposes that OPEFB's lignin subsidiary have the probability for producing good linerboard coating. It gave better waterproof of coated linerboards than the commercial wax coating.

Tanistra and Bodzek (1998) prepared high-purified lignin from black liquor by utilizing ultrafiltration polyacrylonitrile membranes. Accordingly, concentrates enhanced with macromolecular lignin were acquired. Raising the transmembrane pressure, the lignin concentrates of high purity level were gotten.

Wallberg *et al.* (2003) separated lignin from the cellulose during kraft pulping by ultrafiltration and dialfiltration. The result shows the lignin purity to be 36% in the original kraft black liquor that was separated by ultrafiltration and 78% the purity lignin was given after semi-continuous dialfiltration.

Nada *et al.* (1998) separated lignin from black liquor in 5 pulping processes: soda pulping, kraft pulping, sulfite pulping, butanol-water pulping and peroxyformic pulping. Subsequently, lignin could be precipitated from kraft and soda black liquor by using 5% sulfuric acid at pH 2-3. Lignin was precipitated from sulfite black liquor by using methyl alcohol to isolate lignosulfonate.

Perissotto *et al.* (2000) separated lignin from eucalyptus kraft pulping by using of acetone:water and dioxane:HCl 0.1 M. A detailed structural characterization of the kraft pulp extracts by FTIR and NMR showed that these brown extractives was the lignin structure.

Lachenal *et al.* (2004) extracted lignin in kraft pulp by enzymatic hydrolysis of starch, acidolysis with dioxne-water-HCl (traditional strategy). The last technique was appeared to extract lignin with a superior yield than for ordinary acidolysis and lower content in impurities than for enzymatic hydrolysis.

Pichainarong (2002) studied the acid precipitation of lignin from black liquor on Eucalyptus based. A technique for two-step precipitation was suggested in this examination. The polysacharide degradation products were removed from black liquor by centrifuge after precipitation at pH5. At that point the pH of black liquor was lessened to pH 1,2,3,4 and 5, respectively, with sulfuric acid. The lignin fraction was described by NMR, IR, and GPC. The results demonstrated that lignin was higher precipitation when pH was lessened. At pH 3, the lignin was recovered around 93.51%. The COD and color were reduced by 80.45% and 98.20 %, respectively.

Rohella *et al.,* (1996) separated lignin from kraft black liquor with acid precipitating at pH 3 and then extracted with solvent and also treated with 72% sulfuric acid. This isolated lignin was high-purified lignin that had activation energy of 29.87 kJ/mol.

Raschip *et al.,* (2011) evaluated the vanillin release from the matrices of mixed xanthan/lignin hydrogels. The new acquired biodegradable polymeric frameworks, containing vanillin, have been characterized by the swelling/ discharge tests, FT-IR and AFM analysis. In FT-IR spectra after consolidation of the aroma, the shifting of the bands at 1615 and 1514 cm^{-1} to higher wavenumbers was observed. It demonstrated that the interactions have occurred between components. The correlation of the considerable number of results managed by the different characterization procedures leads to the conclusion that the 70X/30GL hydrogel slower releases the vanillin aroma more than 90X/10GL one as a result of stronger interactions between matrix and active substance.

Raschip *et al.,* (2013) studied the morphology and thermal behavior of xanthan/lignin hydrogels. It has been accentuated the impact of the lignin type on the hydrogel properties. The hydrogels were gotten by chemical crosslinking, within the sight of epichlorohydrine as a crosslinking. The hydrogels were analyzed by FT-IR, TGA, and DSC spectroscopy. It has been set up that hydrogels have a porous morphology. The particular intermolecular cooperation is stronger in the case of 70xanthan/30AWL hydrogel. The thermal properties of the hydrogels likewise rely upon lignin type. The lowest thermal stability was found in the hydrogel containing lignin with the most elevated substance of practical gatherings.

Błaszczyński *et al.,* (2013) were to set up the silica aerogel using the sol-gel and supercritical drying. The supercritical drying was picked as the best procedure, guaranteeing the best properties of product and designed and planned and manufactured the supercritical dryer stand that permitted drying tests in high pressure and elevated temperature. The obtained silica aerogels showed great transparency.

Grishechko *et al.,* (2013a) prepared the very porous organic aerogels for the first time from a blended lignin–phenol–formaldehyde (LPF) resin. Six different P/L weight proportions and two (L + P)/F weight proportions have been tested, leading most of times to nice and reproducible hydrogels which were manner either supercritically of freeze-dried. The pore-size distributions were found to depend strongly on the initial composition, but not on the strategy of drying. The thermal conductivity of aerogels has been estimated and observed to be negligible in materials combining both high mesopore volume and pore sizes.

Grishechko *et al.,* (2013b) arranged the exceptionally permeable organic aerogels based on tannin and lignin which were set up at steady solid weight fraction and constant pH, but with various tannin/lignin and (tannin+lignin)/formaldehyde weight ratios. A stage chart has been drawn, demonstrating the scope of structures in which nice hydrogels might be acquired. The porosity of the resultant aerogels, dried with supercritical CO_2, has been systematically examined regarding surface area, in spite of the fact that the aerogels remained absolutely mesoporous materials. Estimations of thermal conductivity and mechanical resistance are also given, which are contrasted and those of much more expensive, non- sustainable, aerogels derived from resorcinol–formaldehyde.

Min Zhang *et al.,* (2012) built up another kind of biodegradable composite agarose/HA hydrogel derived from agarose and hyaluronic acid and using the epichlorohydrin (ECH) as the crosslinking agent. The crosslinking structures, thermal stability and pore morphologies of the composite agarose/HA hydrogel were described by FTIR, TGA, and SEM. The composite agarose/HA hydrogel can be controlled by adjusting the component ratios of agarose and HA, with degradation time extending from 4-8 weeks. These findings show that the composite hydrogel has a possible in wound healing and drug delivery.

Laura *et al.,* (2014) built up the hydrogel networks based on agarose and chitosan by utilizing oxidized dextrins as low cytotoxicity crosslinking agents. The impact of the polysaccharide composition and oxidation level of the dextrins in the last characteristics of the network were examined. The results demonstrated that the development of an interpenetrating or a semi-interpenetrating polymer network was principally reliant on a base agarose substance and degree of oxidation of dextrin. Spectroscopic, thermal and swelling analysis investigation uncovered great similarity with an absence of phase separation of polysaccharides at chitosan:agarose proportions of 75:25 and 50:50.

CHAPTER 3

EXPERIMENTAL

1. Materials

Oil palm empty fruit bunches (OPEFB) were provided by the Virgin vegetable oil Co., Ltd., Songkhla, Thailand. Na_2S and NaOH were supplied from L.B. Science Limited Partnership, Songkhla, Thailand. Xanthan gum was obtained from Tariko Co., Ltd., Bangkok, Thailand. Agarose was distributed from Gibthai Co., Ltd., Bangkok, Thailand. The crosslinking agent, epichlorohydrin (ECH) and other chemicals, e.g. sulfuric acid (H_2SO_4) were purchased from S.V. Medico Co. Ltd, Songkhla, Thailand.

2. Instruments

1. Digester Model. RDB-D352 (Nanasiam Intertrade Co., Ltd.)

Figure 3.1 Cooking Digester

2. Digital balance: Sartorius Model. BP-2100S

Figure 3.2 Digital balance

3. Temperature and humidity chamber Model. WTB Binder-KBF 115

Figure 3.3 Temperature and humidity chamber

4. Hot air oven: Memmert Model. ULM 50

Figure 3.4 Hot air oven

5. Magnetic Stirrer: IKA® Model. C-MAG HS 7

Figure 3.5 Magnetic Stirrer

6. Centrifuge: Dynamica Germany Model. Velocity 18R

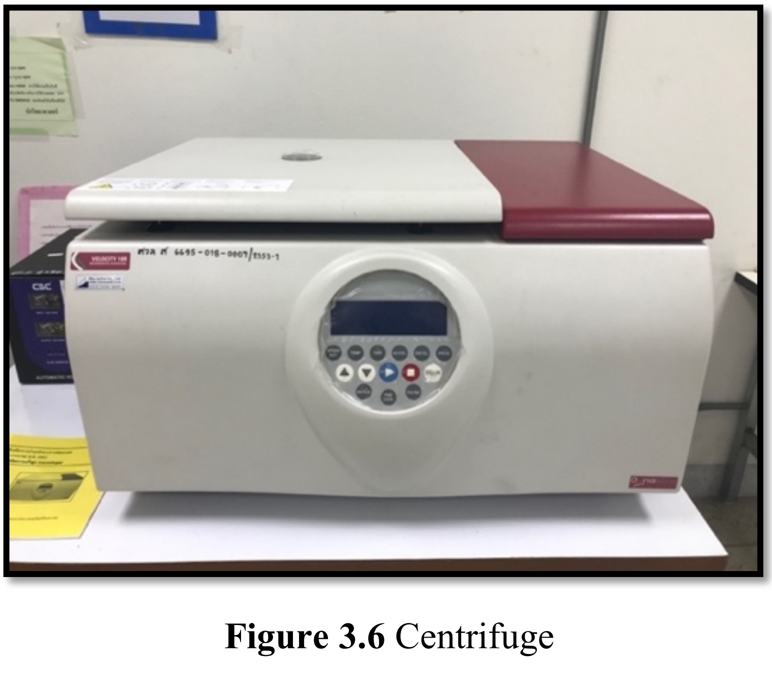


Figure 3.6 Centrifuge

7. pH meter: OHAUS Model. Starter3100

Figure 3.7 pH meter

8. pH Pen: Dymax Medel. ATC-8690

Figure 3.8 pH pen

9. Fourier transform infrared spectrophotometry: BrukerModel.Vertex 70.

Figure 3.9 Fourier transform infrared spectrophotometry (FTIR)

10. Thermogravimetric analyzer: Perkin-Elmer Model. TGA7

Figure 3.10 Thermogravimetric analyzer (TGA)

11. FEI Quanta 600 FEG scanning electron microscope (SEM)

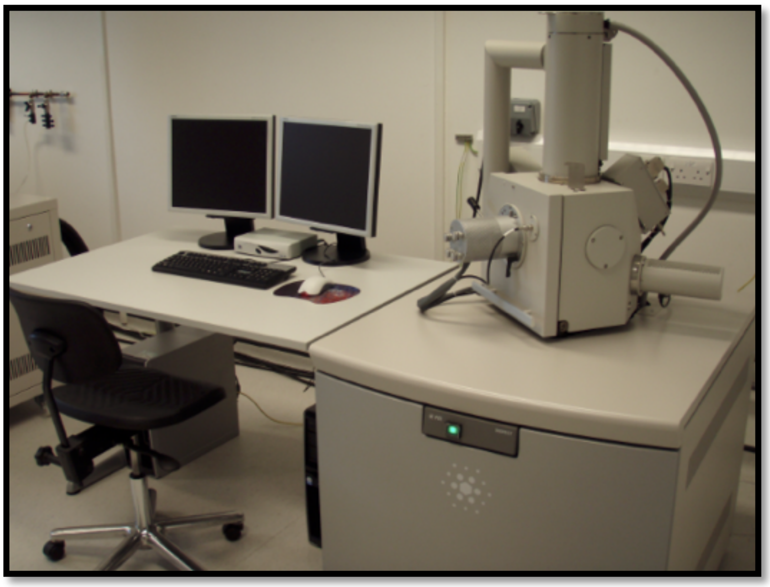


Figure 3.11 Scanning electron microscope (SEM)

12. Gel permeation chromatography:Model PL-GPC 110

Figure 3.12 Gel permeation chromatography (GPC)

13. Gotech Bursting Tester Model. GT-7013AD

Figure 3.13 Bursting Tester

14. Brookfield viscometer DV-II+Pro coupled with S-94 spindle

Figure 3.14 Brookfield viscometer DV-II+Pro

15. Brunauer–Emmitt–Teller ASAP2460 (BET, Micromeritics, U.S.A.)

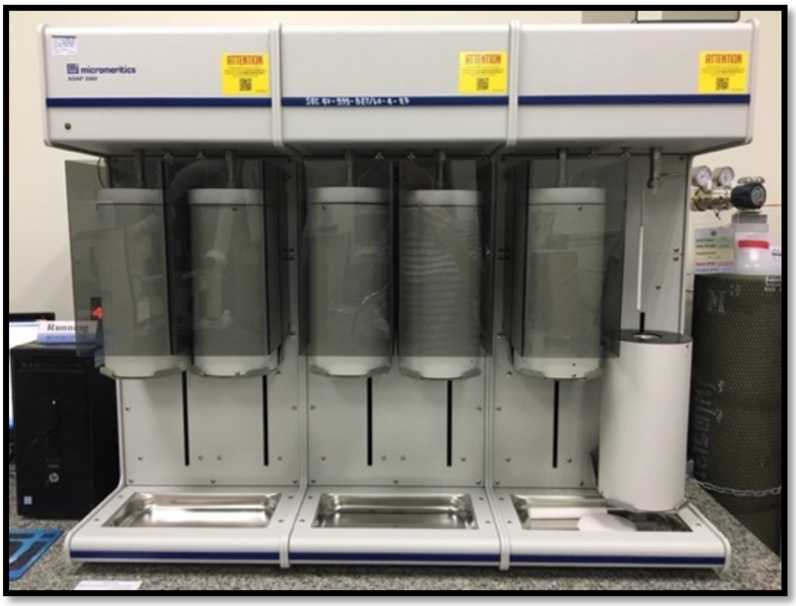


Figure 3.15 Brunauer–Emmitt–Teller

16. True Density Analyzer (AccuPyc II 1340, Micromeritics, U.S.A.)

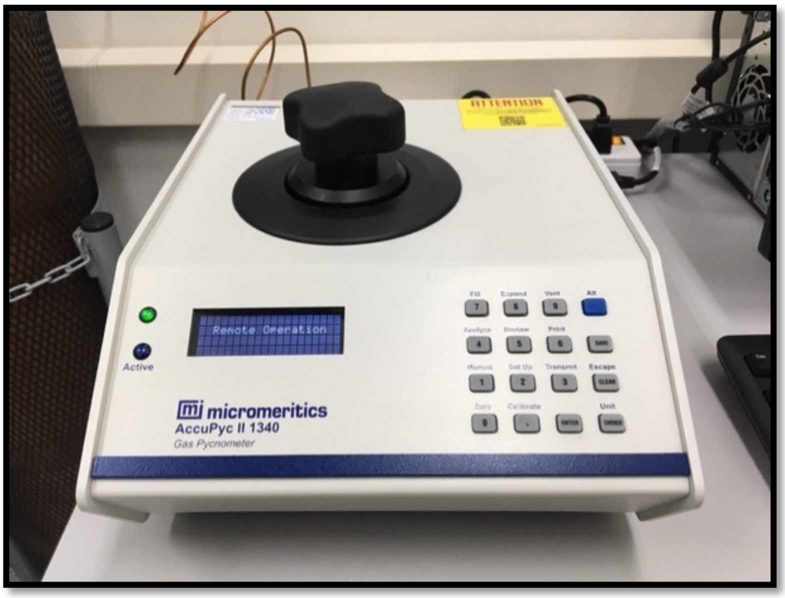


Figure 3.16 True Density Analyzer

17. Universal material testing machine: LLOYD Model LR30K.

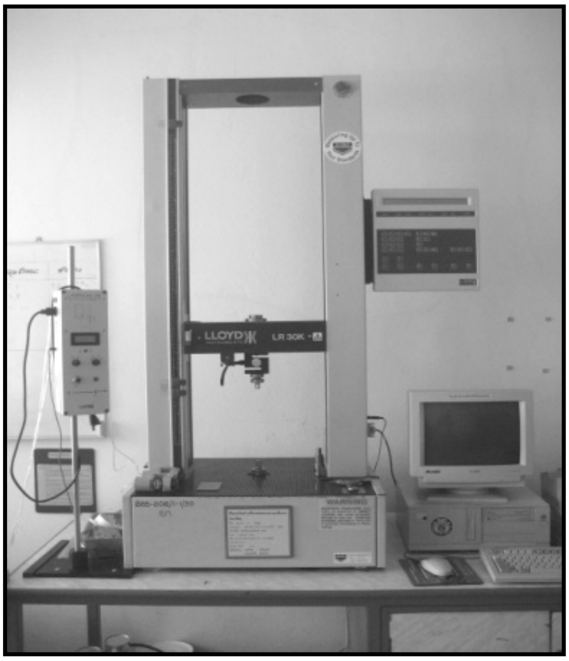


Figure 3.17 Universal material testing machine

18. Differential Scanning Calorimeter: Perkin-Elmer Model DSC8500.

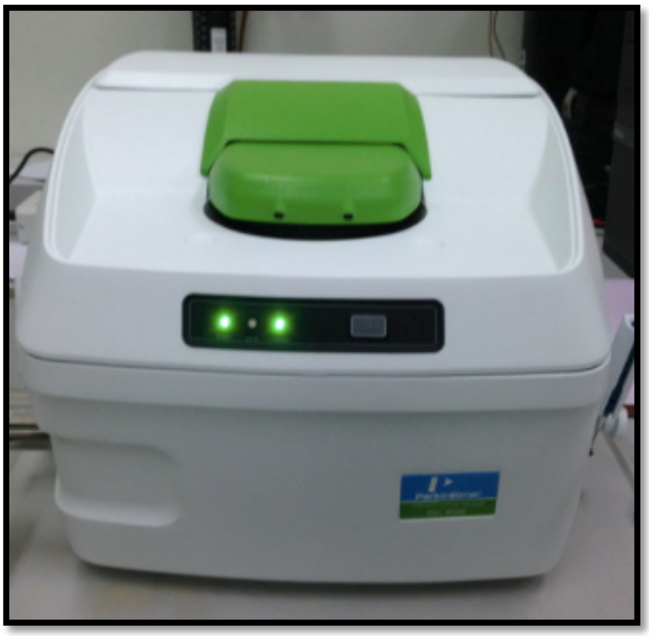


Figure 3.18 Differential Scanning Calorimeter

19. Texture analyzer (TA.XT Plus, Godalming, UK)

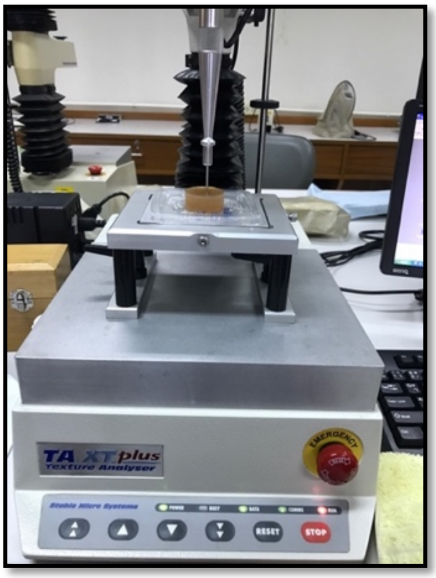


Figure 3.19 Texture analyzer

3. Methodology

3.1 Pulping process

3.1.1 Kraft pulping process

Oil palm empty fruit bunches (OPEFB) were cut into small pieces and washed with clean water 3-5 times, then dried in a hot air oven for at least 48 hours. The OPEFB and cooking liquor (1:10 w/v) were cooked in a digester for 180 minutes. The Response Surface Methodology (RSM) and the multiple regression analysis used to study the optimal condition of kraft pulping process from OPEFB. The Graphical method (Superimposition) was shown in Table 3.

Table 3.1 The operational variables of kraft pulping process with OPEFB.

Experimental No.	Effective alkali (%)	Sulfidity (%)	Temperature (^{O}C)	Liquor ratio (w/v)
1	1(30)	1(40)	0(160)	1 : 10
2	1(30)	-1(20)	0(160)	1 : 10
3	-1(20)	1(40)	0(160)	1 : 10
4	-1(20)	-1(20)	0(160)	1 : 10
5	1(30)	0(30)	1(180)	1 : 10
6	1(30)	0(30)	-1(140)	1 : 10
7	-1(20)	0(30)	1(180)	1 : 10
8	-1(20)	0(30)	-1(140)	1 : 10
9	0(25)	1(40)	1(180)	1 : 10
10	0(25)	1(40)	-1(140)	1 : 10
11	0(25)	-1(20)	1(160)	1 : 10
12	0(25)	-1(20)	-1(140)	1 : 10
13	0(25)	0(30)	0(160)	1 : 10
14	0(25)	1(40)	0(160)	1 : 10
15	0(25)	0(30)	1(180)	1 : 10

After these operations, the precipitated pulp was washed with water. The black liquor was separated through a strainer and afterward was stored at room temperature for 24 hours. After that, the COD and pH value of the black liquor was measured.

3.1.2 Soda pulping process

The OPEFB and 20% NaOH solution (1:15 w/v) was cooked in the digester with the temperature at 170°C for 180 minutes. Black liquor got from the cooking was kept at room temperature for 48 hours. After that, the pH value and COD of the black liquor, taken from the digester at the end of cooking, was measured. This method was followed by the commercial soda process of three paper mills in Peninsular Malaysia (Rushdan *et al.* 2007).

3.2 Testing of mechanical properties of pulp obtained from kraft and soda pulping

3.2.1 Preparation of pulping sheet

After cooling, the fibers were separated by a wire mesh test sieve. The black liquor was permitted to move through the mesh. After filtration, they are left with brown stock. The brown stock was altogether washed with water several times for 40 minutes to remove black liquor and excess alkali. The washed pulp was subjected to the screener. Screening is achieved to separate the pulp into accepts and rejects. The pulp sheets of 160 g/m^2 were produced.

3.2.2 Tensile strength test

The tensile and ring crush properties of paper were evaluated with a Universal Testing Machine. The tensile test was achieved by TAPPI T494. The distance between clamps was fixed at 10 cm and using a strain rate at 15mm/min. The tensile strength was reported as the tensile index (TI) which calculated by the basis weight of the specimen.

3.2.3 Ring crush test

The ring crush test was also performed following TAPPI T818. A specimen (6in.×0.5in.) was set in a circular block, and after that compressive force was connected to the specimen center of the plate and pressed with the rate of 0.5 in./min. The ring crush index (RCI) were divided by the basis weight of the specimen as to avoid the effect of different thicknesses.

3.2.4 Burst test

The bursting tester was utilized to decide the bursting strength of paper. The specimen (at least 4in.×4in) was embedded between the clamping ring and diaphragm plate. Afterward, 100 psi of pneumatic pressure was applied to the specimen until the point that its burst. The bursting strength was reported as the bursting index (BI).

3.2.5 Statistical data analysis

All mechanical properties of paper were determined at least six replicates. The mean and standard deviations were calculated and reported. Analysis of variance (ANOVA) was operated by using Duncan's new multiple range test (DMRT) to decide the significant differences of paper properties. All significant values were expressed at 95% confidence level.

3.3 Separation of lignin from black liquor

Black liquor was filtered through a white cloth and adjusted to pH 6 with concentrated sulfuric acid. The sludge was separated from the black liquor by centrifugation. After that, the pH of black liquor was altered to different levels, e.g. 4, 3, and 2. The pH adjustment was done by the addition of sulfuric acid and then was stored at ambient temperature for 24 hours. After that, 40 ml of sample was transferred to the centrifugal tube and centrifuged to separate the liquid from solids at 13000 rpm for 15 min. The precipitated lignin was then washed with distilled water until a neutral pH. Lignin was removed from the centrifugal tube and dried in a hot air oven for at least 24 hours. The purity of lignin was investigated by the determination of acid-insoluble (Klason) lignin in pulp with gravity method.

3.4 Analysis of lignin

The recovery yield of each lignin fraction obtained from different pH separations was computed as follows:

$$\%\, lignin\ yield = \left(\frac{W_1}{W_2}\right) \times 100$$

When W_1 is the weight of the recovered lignin and W_2 is the weight of the OPEFBs used for the extraction.

The COD of the effluent was relegated by dichromate open reflux technique according to standard methods for examination of water and wastewater, 21st edition 2005. The initial color of the effluent is highly dark brown, that is the reason to estimate by making its dilution by three times.

The purity of the recovered lignin was investigated by the determination of acid-insoluble (Klason) lignin in pulp with gravity method. The official method T222-om-02 was used to measure the amount of lignin in the black liquor.

The lignin compositons were investigated by an infrared spectrometer using the Fourier transform infrared spectrophotometry (FTIR). The KBr pellet technique utilized for setting up the samples. All spectrums were recorded in a frequency range of 400–4000 cm^{-1}.

The thermal behavior of lignin fractions was contemplated by utilizing a thermogravimetric analyzer. Outputs were recorded from 50 to 850°C with a heating rate of 10°C/min under a nitrogen atmosphere.

DSC analyses were proceeded under the nitrogen atmosphere with heating (using a Perkin Elmer DSC8500). Approximately 10 mg of lignin sample was stored and sealed with aluminum in an aluminum pan. An empty aluminum pan was the reference. The samples under the nitrogen atmosphere were heated from -30 to 450°C with a heating rate of 10°C/min.

The molecular weight distribution of the lignin was determined using gel permeation chromatography (GPC) (Waters Series 1515). Monodisperse polystyrene was used as the standard. The sample was completely dissolved in Tetrahydrofuran (THF) (5 mg/mL). The GPC calibration is performed with PS standards (polystyrene).

3.5 Gum-lignin aerogels

3.5.1 Preparation of lignin solution

Lignin powder around 50g were dissolved in 200 mL of distilled water and stirred at 85 °C for an hour. Meanwhile, 15 mL of 30 wt.% NaOH solution was added to this mixture until the final pH was 12. A dark homogeneous solution having a lignin concentration of 20 wt.% was obtained. This solution is used to prepare each gel after cooling at room temperature.

3.5.2 Preparation of gum solution

3.5.2.1 Agarose solution

Agarose solutions with the concentration of 1%, 3%, and 5% (w/v) were prepared by dispersing agarose in distilled water and heating the solutions to 68±2 °C for 30 minutes. The solution was continuously stirred and the appropriate amount of lignin solutions (1%, 3%, and 5%w/v) were added to the agarose solution under constant stirring at 120 rpm. The lignin-agarose solutions were mixed rapidly with the cross-linking agent (epichlorohydrin; ECH). ECH was added each one mL till to 10 mL of composite solutions. Then, they were further stirred at 120 rpm for 30 min. The solvent evaporation during stirring was minimized by covering the beaker with a plastic film. The mixtures were poured into the Petri dish and then cooled to the ambient temperature before peeling the hydrogel off the plates.

3.5.2.2 Xanthan solution

Xanthan gum solutions were set up by dissolving of 1% w/v xanthan gum in distilled water. The solution was continuously stirred and the appropriate amount of lignin solutions (3% w/v) were added to the agarose solution. ECH was filled up slowly until to 10 mL. Samples were stirred at room temperature with a steady mixing rate of 150 rpm for at least 24 hours. The mixtures were poured into the Petri dish and then cooled to the ambient temperature.

3.5.3 Preparation of gum-lignin hydrogels

All hydrogels have been prepared in the petri dish. Mono- and multicomponent hydrogels have been produced by pouring the solutions into the petri dish and allowing the solution to cool down to room temperature. Samples were cut into the circle pieces whose dimensions, typically $4\pi \mathrm{cm}^2 \times 1\mathrm{cm}$. The samples were cooled at 3°C for at least 24 hours. All samples were sealed with Parafilm® to avoid water evaporation during storage. The hydrogels were removed from the cooler an hour before measurements.

3.5.4 Preparation of gum-lignin aerogels

The hydrogels were removed from the petri dish were cut into the cubic pieces with a typical size of 5mm×5mm×5mm. After that, the pieces of hydrogels were dehydrated with the supercritical drying (CPD) and freeze drying (FD).

3.6 Characterization of gum-lignin aerogels

3.6.1 The viscosity of lignin-xanthan hydrogel

Viscosity of the in situ gel systems was determined using Brookfield viscometer DV-II+Pro coupled with S-94 spindle (Brookfield Engineering Laboratories Inc., MA, USA). The prepared gel formulations were transferred to the beaker. The spindle was lowered perpendicularly into the gel at l00 rpm and temperature was maintained at 25 ± 0.5 °C. The viscosity was determined during the cooling of the system (Shinde et al., 2008). All the measurements were performed in triplicates.

3.6.2 Texture analysis of lignin-agarose hydrogels

The penetration tests were using a texture analyzer (TA.XT Plus, Stable Micro Systems, Ltd., Godalming, UK) installed with a 2 mm diameter stainless steel needle probe and a 5 kg loading cell. The hydrogel was punched at its center positions by the needle and recorded the compression force. The preferment rate of a needle was 0.1mm/s, and the maximum strain lets were 80%. A recording rate of 600 points/s and takes about 120 seconds to be completed. All the hydrogels were repeated triply, and results were shown in average values, with the standard deviation of data.

3.6.3 Morphology and functional groups of gum-lignin aerogels

The aerogels morphology was examined by using an FEI Quanta 600 FEG scanning electron microscope (SEM). The selection of aerogels having different gel precursors and drying methods were investigated the morphology and functional groups of composited aerogels.

Chemical differences among organic gels were determined by using the Fourier transform infrared spectrophotometry (FTIR). The results were investigated by the Scientific Equipment Center, Prince of Songkla University.

3.6.4 Density and porosity of gum-lignin aerogels

The specific surface area and porosity analyzer of aerogels were examined by Brunauer–Emmitt–Teller (BET) method (BET, Micromeritics, U.S.A.) with True Density Analyzer (AccuPyc II 1340, Micromeritics, U.S.A.). BET-surface area and adsorption average pore diameter of the aerogels were determined from nitrogen adsorption–desorption isotherms on an ASAP2460. The results were analyzed by the Scientific Equipment Center, Prince of Songkla University.

4. Economic analysis

The initial phase of the assessment of any procedure comprises in studying the Strengths–Weaknesses–Opportunities–Threats (SWOT) framework. This framework incorporates the results of an external survey, which decides the opportunities and threats of the procedure inside the genuine market. An internal survey, which was decided on the strengths and weaknesses of the process in comparison to those of the participants. The assessment of the SWOT framework permits to determine the attentiveness of the procedure or the need to upgrade different features prior to its detailed economic evaluation. If the conclusion from the SWOT framework is favorable, the accompanying advance involves the investment analysis, which incorporates the estimation of the equipment cost required for the procedure and afterward the total capital investment of this research (Román *et al*., 2015).

5. The expenditure

Financial support received from the Graduate School at Prince of Songkla University and the Strategic Scholarships Fellowships Frontier Research Networks (Specific for Southern region).

6. Research laboratories and storage

- Department of Material Product Technology, Faculty of Agro-Industry, Prince of Songkla University, Hatyai, Songkhla, Thailand.
- Laboratory center, Faculty of Environmental Management, Prince of Songkla University, Hatyai, Songkhla, Thailand.
- Scientific Equipment Center, Prince of Songkla University, Hatyai, Songkhla, Thailand.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Pulping process

Despite having many publications about the properties of soda pulp sheets from OPEFB, there is a little information on the properties of OPEFB pulp sheets made from the kraft pulping process. For this reason, the properties of sulfate pulp sheets were studied such as tensile index, ring crush index, and burst index. Also, the lignin recovery from kraft black liquor of OPEFB was determined by the acidic process.

4.1.1 Testing of mechanical properties of pulp obtained from kraft and soda pulping

Fifteen conditions of OPEFB kraft pulping were trialed to measure the optimal condition, as following the Box and benkhen design. Some mechanical properties of pulp sheets have been investigated to identify the optimal conditions of OPEFB pulping. The properties of kraft pulp sheets were compared to the soda pulp sheets of OPEFB.

4.1.1.1 Ring crush index (RCI)

A ring crush test is often used as a standard method for testing the compressive strength of corrugated container (Nordstrand, 2003). The ring crush indices (RCI) of pulp sheets obtained from kraft 7, karft 12 and kraft 15 have the higher compressing force, in Figure 4.1. They contributed the highest RCI which was about 0.24-0.26 Nm/g. In contrast, the RCI of pulp sheets obtained from soda pulping was the lowest.

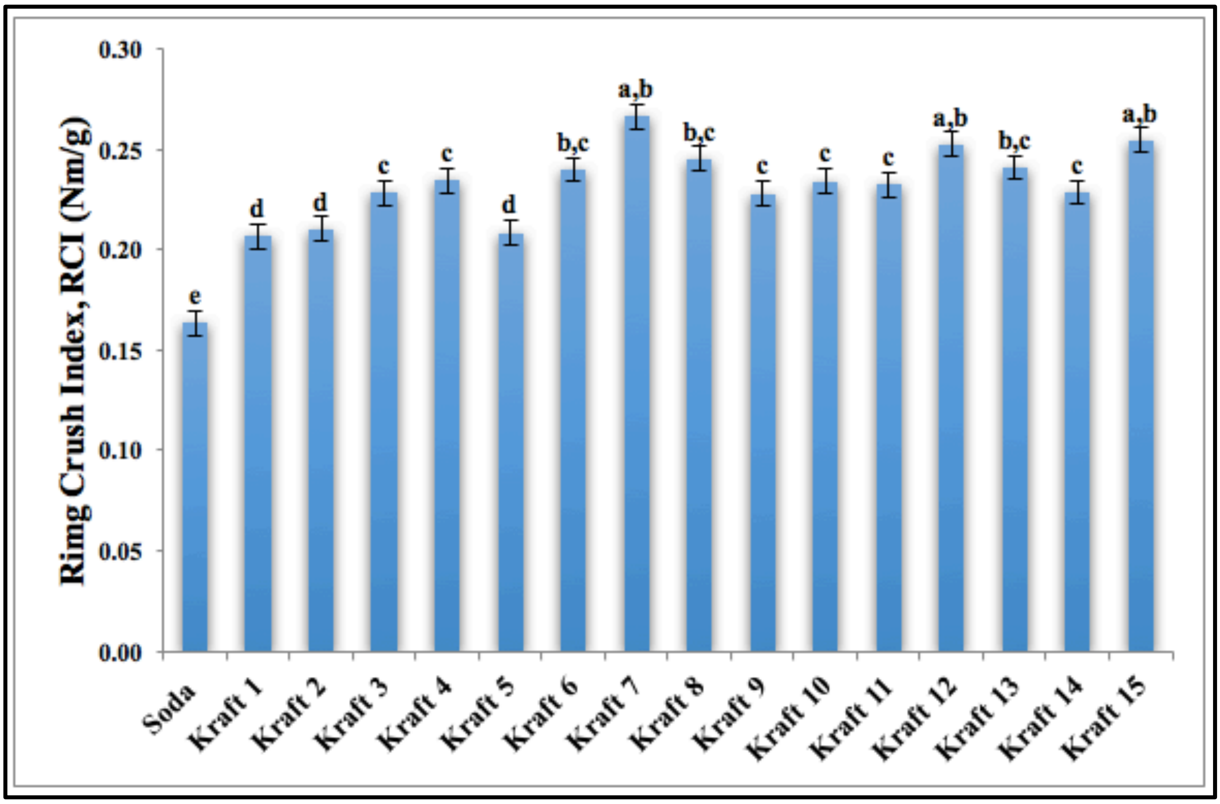


Figure 4.1 Ring crush Indices of pulp sheets obtained from kraft and soda pulping.

Notes : Mean values with different letter are significantly different ($p < 0.05$).

4.1.1.2 Tensile index (TI)

Tensile testing was an important step in the analysis of the mechanical strength of the various paper product. Tensile index (TI) is a measure of the material resistance under fracture stress. It depends on the strength, length and surface area of the fibers and the strength of bonding between them (Hirn *et al.*, 2015 and Araújo *et al.*, 2013). The results demonstrated that a maximum tensile index (TI) of pulp sheets obtained from kraft15 was 6.58 Nm/g. Tensile indices of kraft pulp sheets were higher than soda pulp sheets (2.74 Nm/g). The results of tensile indices are illustrated in Figure 4.2.

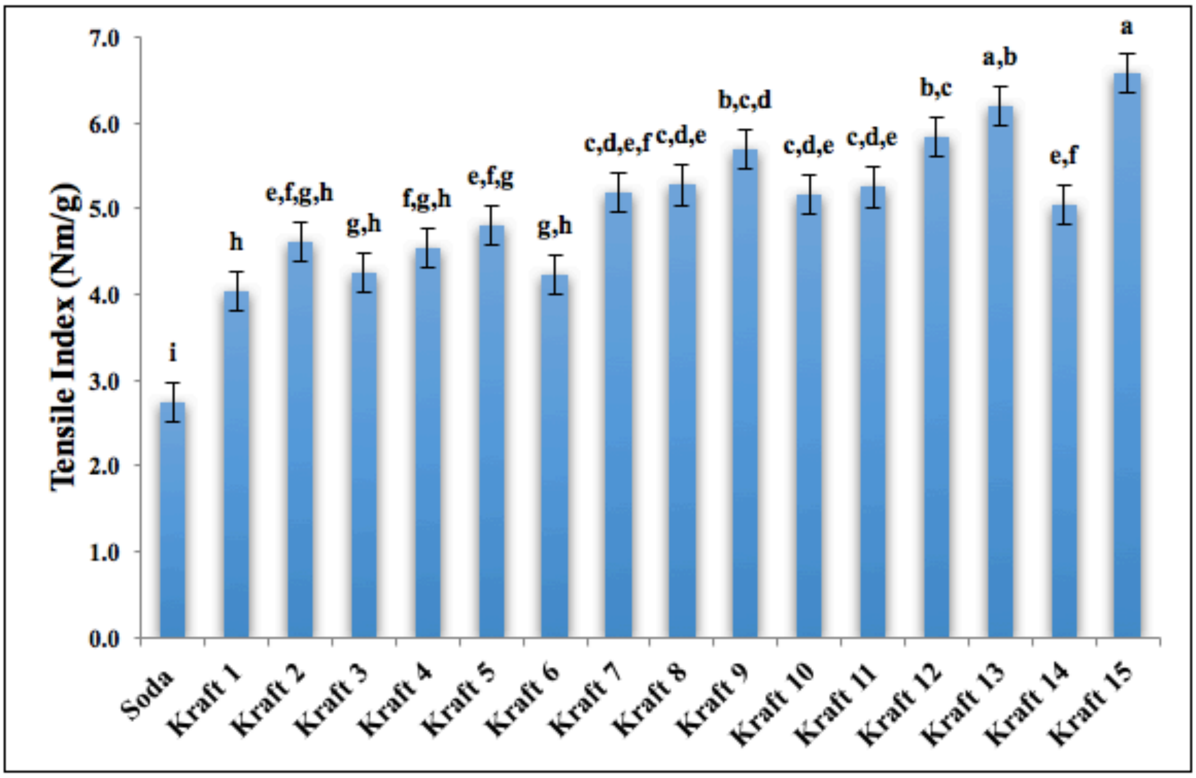


Figure 4.2 Tensile indices of pulp sheets obtained from kraft and soda pulping.

Notes : Mean values with different letter are significantly different ($p < 0.05$).

4.1.1.3 Burst index (BI)

The trend of burst index (BI) was observed to be similar to that of the tensile index. Burst testing is the method to evaluate the usability and behavior of paper when the perpendicular forces to the surface. It can indicate the rupture resistance of paper materials (Haslach, 2000). Burst indices of pulp sheets produced from kraft pulping were higher than soda pulp sheets (0.60 kPa.m^2/g). The pulp sheets of kraft7 revealed the greatest burst index (BI) of 1.43 kPa.m^2/g, shown in Figure 4.3.

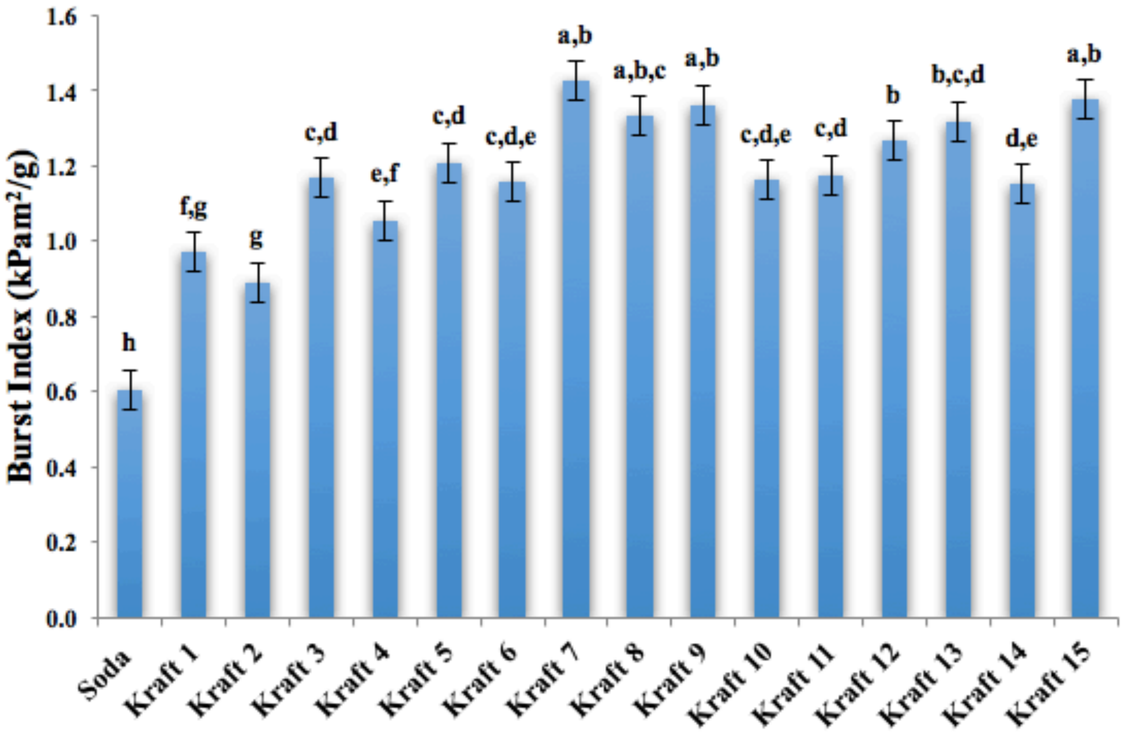


Figure 4.3 Burst indices of pulp obtained from kraft and soda pulping.

Notes : Mean values with different letter are significantly different ($p < 0.05$).

The mechanical properties of pulp sheets from kraft pulping were greater than soda pulping due to the higher delignification of kraft pulping has effected to the mechanical properties of pulp sheets, as corresponding to the results from others research (Epelde *et al.*, 1998 and Knoblauch *et al.*, 2000).

Black liquor is a byproduct from the chemical pulping process when cooked the wood chips into pulps. Kraft process dissolved lignin, hemicelluloses and other extractives from the wood with sodium based alkali compounds, such as sodium sulfide and sodium hydroxide (Enkvist and Alfredsson, 1953). After precipitation with acid from the black liquor, sulphate lignin is separated.

The crudes lignins separated from the black liquor after precipitation by acid at pH6, were about 16 - 25 % of the initial wood mass that demonstrated in Figure 4.4, as corresponding to the results from others research (Vasileva and Gushterova, 2007, Nenkova, 2007, and Narapakdeesakul *et al.*, 2013). The sulfide compound is a catalyst for the decomposition of lignin from the wood without causing degradation of cellulose. The breakdown of ether bond on the lignin side chain has an important role in separating the lignin from the wood.

The mechanism of the soda pulping process is different from kraft pulping. Sodium hydroxy (NaOH) was as an additive to swell hemicellulose within the pulp fiber. It increased the surface area and decreased the crystallization of the cellulose. Moreover, it and reduced the size of the polymer which make it possible to separate the lignin from wood. Hydroxyl ions act as nucleophilic, resulting in the breakdown of the ether bond. The breakdown of the ether bond of lignin are important for extraction of lignin from the wood.

On the other hand, the main chemical of the kraft pulping process is sulfide which accelerates the decomposition of lignin from wood without degradation of cellulose. The combination of hydrosulfide and sulfide ion is a nucleophilic resulted in the breakdown of the ether bond rather than the hydroxyl ion. Lignin can be separated from the wood rather than the soda pulping process.

Berg and Pickering (2007) reported that the pulp with higher amounts of residual lignin led to be poorer mechanical properties and increased to decay when subjected to accelerated deterioration testing.

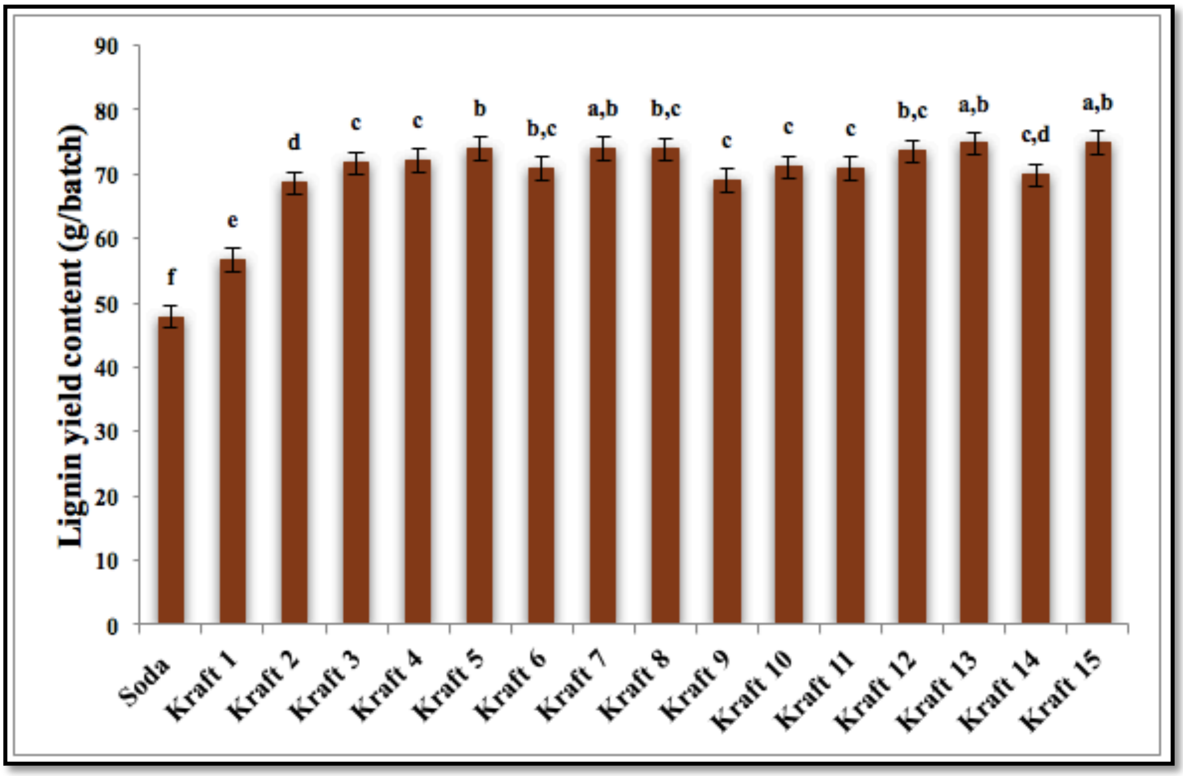


Figure 4.4 Lignin yield of the black liquor from alkaline pulping process after precipitation by acid at pH6.

4.2 Separation of Lignin from Black Liquor

The optimal condition of lignin separation from kraft black liquor was studied by the acidic process. OPEFB lignins were obtained by precipitation at pH 2, 3, and 4. The yield and purity of isolated lignins were shown in Table 4.1. The results of COD analysis were also shown in Table 4.1.

Table 4.1 Yield, and purity of the precipitated lignins and COD of black liquor.

Conditions	pH	COD (mg/L)	% yield of lignin	Purity of lignin
Soda	pH2	5,019	20.34	30.18 ± 2.58
	pH3	5,057	21.95	34.65 ± 0.62
	pH4	4,868	18.10	34.12 ± 0.24
Kraft 1	pH2	2,815	25.94	77.79 ± 0.09
	pH3	2,778	28.71	81.14 ± 3.14
	pH4	2,665	26.14	79.25 ± 0.07
Kraft 2	pH2	3,786	24.90	61.79 ± 0.09
	pH3	3,655	25.13	63.42 ± 0.07
	pH4	3,142	29.15	70.02 ± 4.27
Kraft 3	pH2	3,682	25.03	69.98 ± 1.08
	pH3	4,000	26.13	74.65 ± 4.38
	pH4	3,860	30.10	78.60 ± 1.56
Kraft 4	pH2	3,256	26.08	75.45 ± 4.38
	pH3	2,680	27.03	81.64 ± 2.44
	pH4	3,010	29.10	80.13 ± 0.76
Kraft 5	pH2	3,290	25.55	81.38 ± 0.38
	pH3	3,680	28.44	83.92 ± 0.21
	pH4	3,344	24.98	80.62 ± 3.14
Kraft 6	pH2	3,460	20.40	74.78 ± 1.56
	pH3	3,365	27.24	79.55 ± 2.38
	pH4	3,940	30.48	79.04 ± 0.86
Kraft 7	pH2	4,333	24.40	81.45 ± 2.03
	pH3	3,665	31.35	89.64 ± 0.02
	pH4	3,268	28.15	86.13 ± 0.08
Kraft 8	pH2	2,683	23.25	83.88 ± 0.18
	pH3	3,105	31.08	89.29 ± 0.18
	pH4	2,894	26.65	85.12 ± 1.44

Conditions	pH	COD (mg/L)	% yield of lignin	Purity of lignin
Kraft 9	pH2	2,185	27.20	82.08 ± 0.56
	pH3	2,665	29.19	88.35 ± 0.38
	pH4	2,344	25.67	86.54 ± 0.06
Kraft 10	pH2	2,685	25.20	78.65 ± 1.33
	pH3	2,915	29.88	84.21 ± 0.12
	pH4	2,704	28.42	82.47 ± 0.05
Kraft 11	pH2	2,667	27.22	76.11 ± 1.33
	pH3	2,414	29.83	78.04 ± 2.17
	pH4	2,532	31.02	74.66 ± 0.02
Kraft 12	pH2	2,960	29.22	88.18 ± 4.58
	pH3	3,114	30.81	90.58 ± 4.58
	pH4	3,097	26.02	85.49 ± 4.14
Kraft 13	pH2	2,963	27.72	79.68 ± 5.56
	pH3	3,444	31.32	85.95 ± 2.08
	pH4	3,021	30.01	82.61 ± 4.06
Kraft 14	pH2	2,772	28.92	80.12 ± 5.56
	pH3	2,890	29.44	86.14 ± 2.67
	pH4	3,001	30.19	82.03 ± 4.08
Kraft 15	pH2	2,755	28.00	84.68 ± 5.56
	pH3	2,984	31.92	90.02 ± 5.40
	pH4	2,647	29.54	86.52 ± 2.04

Lignin obtained from the soda process was compared to the kraft process. The percentage of lignin obtained from the soda process, about 10%, is less than the kraft process. The lignin purity of the soda process is less than the kraft process of about 50-60%. Due to the kraft process can be delignified better than the soda process, the COD of black liquor obtained from the kraft process was lower than the soda process. It showed that the waste water from kraft process after lignin isolation had been environmentally friendly.

The purity of lignin was used to evaluate the influence of the main cooking parameters in the kraft pulping of OPEFB. Regression analysis was conducted for fitting the following order polynomial equation:

pH 2 ; $Y = 563.017 - 2.344X_1 + 3.728X_2\ 4.992X_3\ 0.107X_1X_2\ 0.010X_1X_3\ 0.028X_1^2$ $0.146\ X_2^2 + 0.011X_3^2$

pH 3 ; $Y = 436.519 - 4.513X_1 - 5.801X_2\ 4.358X_3\ 0.124X_1X_2\ 0.026X_1X_3\ 0.042X_1^2$ $0.279\ X_2^2 + 0.009X_3^2$

pH 4 ; $Y = 436.519 - 4.513X_1 - 5.801X_2\ 4.358X_3\ 0.124X_1X_2\ 0.026X_1X_3\ 0.042X_1^2$ $0.279\ X_2^2 + 0.009X_3^2$

Where Y is the purity of lignin at pH2, pH3 and pH4 of kraft pulping. X_1, X_2 and X_3 are the sulfidity, EA and cooking temperature, respectively.

The correlation coefficient for the purity of lignin at pH 2, pH 3 and pH 4 were 90.57%, 96.55% and 93.66%, respectively. The effects of the cooking conditions on the purity of lignin is clearly shown in Figure 3. The purity of lignin at pH 2, pH 3 and pH 4 were 89.21%, 93.97% and 87.488%, respectively. The optimum conditions to achieve the above responses are a cooking time of 180 min, a cooking temperature of 140°C, sulfidity of 21.5 and EA of 21.6.

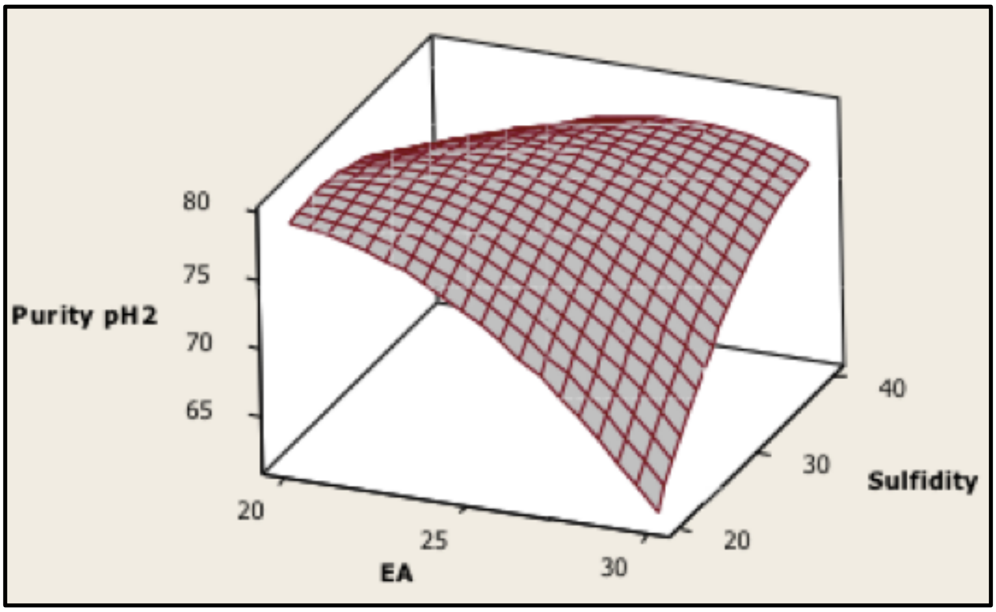


Figure 4.5 Effects of Sulfidity and EA on the purity of OPEFB pulp at 160 ºC of cooking time for pH 2.

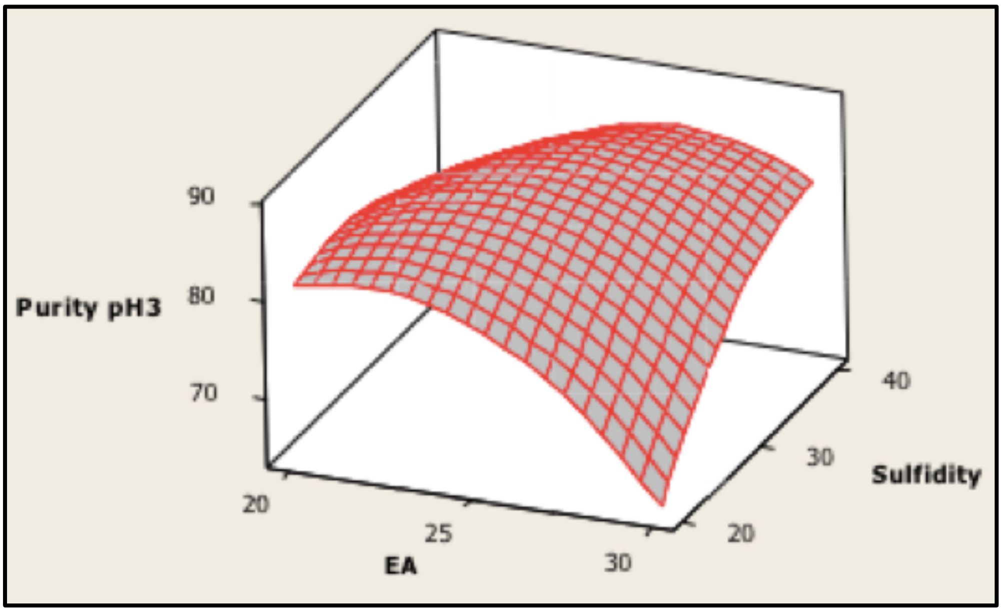


Figure 4.6 Effects of Sulfidity and EA on the purity of OPEFB pulp at 160 ºC of cooking time for pH 3.

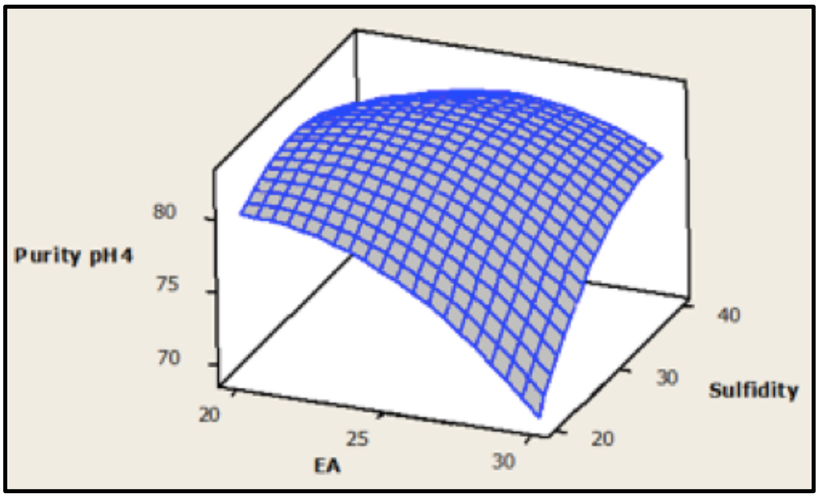


Figure 4.7 Effects of Sulfidity and EA on the purity of OPEFB pulp at 160 ºC of cooking time for pH 4.

Results from the regression analysis showed that the yield was affected mainly by the cooking temperature followed by the chemical charge concentration. Figure 4.5, 4.6, and 4.7 illustrates the relationship between the variables in the quadratic model of purity of lignin. The values of the regression coefficient of the sulfidity and EA indicated that the purity of lignin increased with decreasing of the sulfidity and EA. At a certain of the sulfidity level and EA level, the purity of lignin is not increased. There was an optimal value for this variable.

The kraft lignin from the optimum conditions was precipitated by sulfuric acid addition. The acid precipitation is the most well-known technique used to recover kraft lignin from black liquors. Lignin precipitation was completely when the pH is reduced to a range of 5–1 (Garcia-González *et al.*, 2009). The yield and purity of lignin precipitation at different pH levels are demonstrated in Table 2. They are influenced by the pH precipitation. It was shown that the lower pH is likely to encourage retrieval of lignin from the kraft black liquor (Garcia-González *et al.*, 2009 and Sun *et al.*, 2001).

Table 4.2 Yield, and purity of the precipitated lignin and COD of black liquor.

pH	Yield of lignin* (%)	Purity of lignin (%)	COD (mg/L)
Controlled (12.1)	14.17 ± 1.04	48.76 ± 2.71	6870
5.0	25.10 ± 1.26	80.62 ± 0.51	3213
4.0	24.90 ± 0.82	86.54 ± 0.06	2984
3.0	26.02 ± 0.24	90.35 ± 0.38	3105
2.0	20.34 ± 0.64	82.08 ± 0.56	2667
1.0	22.59 ± 0.48	78.65 ± 1.06	2865

*Based on total dry solid of black liquor.

As shown in Table 2, the isolated lignin from kraft black liquor of OPEFBs showed the greater intensity at pH 3.0. It contributed the highest yield and purity as 26.02% and 90.35%, respectively. In contrast, the precipitation at pH 2.0 and pH 1.0 gave the lowest lignin yield and less amount of impurities, respectively. As would be expected, the yield and the purity of lignin depended on the pH precipitation and composition of the raw materials, which was consistent with other reports (Gilarranz *et al.*, 1999, Sun *et al.*, 1999, Garcia-González *et al.*, 2009, and Methacanon *et al.*, 2010).

Effect of pH on the decreasing of chemical oxygen demand (COD) of wastewater was observed to be noteworthy. COD reduction was up to 38% at pH 2. The color analysis also showed a tendency to decrease color in the water after lignin separation. The yield of lignin and COD were similar at pH 5-1 because lignin is an organic substance that makes the wastewater to the dark color. When lignin is separated from the black liquor, COD was reduced. The results were consistent with other researches (Gilarranz *et al.*, 1999, Garcia-González *et al.*, 2009, and Methacanon *et al.*, 2010)

The reduction of COD is important for wastewater treatment due to the higher COD levels mean a more considerable amount of oxidizable organic material in wastewater. These substances should be reduced to a minimum in the wastewater treatment plant that can make it an attractive option for the treatment of industries wastewater.

Furthermore, the color of the black liquor was changed with lower pH. It changed from dark brown color to light yellow when the pH of the liquor decreased from 5 to 2 (Figure 4.8). The dark brown liquor is derived from the chromopholic groups in the structure of lignin such as carbonyl groups, carboxylic acids, quinones, phenolic hydroxyl groups and hydroperoxy radicals, which are soluble in alkaline. The results are similar to those of other researchers, such as Pichainarong, (2002) and Mussatto *et al*., (2007).

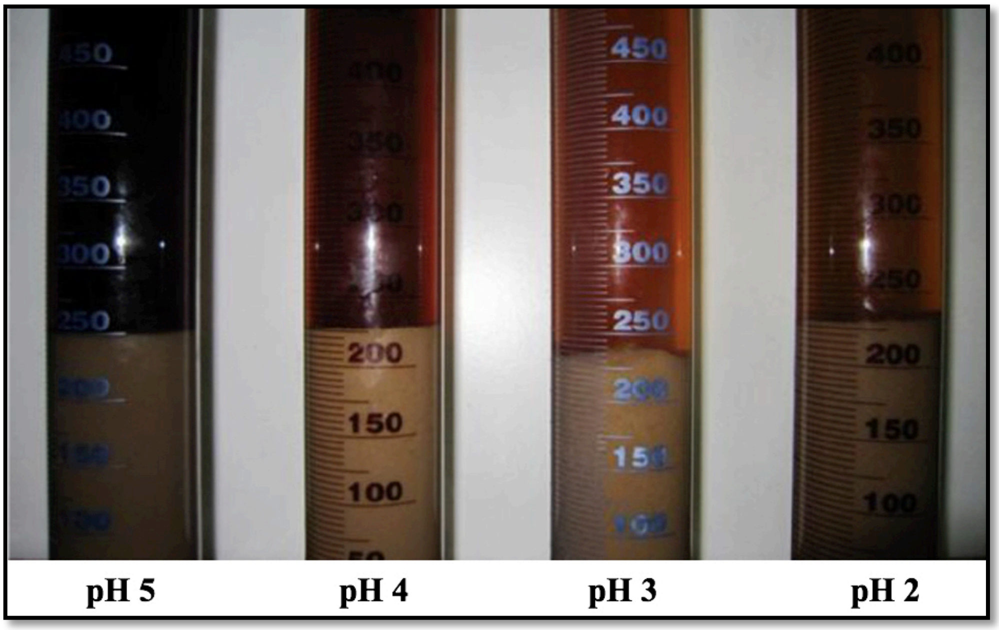


Figure 4.8 The physical characteristics of the black liquor at different pH (5, 4, 3 and 2).

It is also found that lignin can be easily precipitated at the higher acidity, leading to the color of liquor become lighter. This phenomenon supports that the recovery of lignin increased with decreasing the acidity of black liquor.

The FTIR spectrums of all isolated lignin samples were very similar, especially core structure of lignin (shown in Figure 4.9 and Table 4.3). The band at 3146 cm^{-1} assigned to the –OH groups of the physically absorbed water or bonded in aliphatic and aromatic groups. The band at 2923 cm^{-1} was attributed to C-H stretching in aromatic methoxyl or methylene groups of side chains. The band at 2852 cm^{-1} was assignable to vibration of methyl group or methoxyl. The band at 1692 cm^{-1} coincided to conjugated carbonyl groups, but two bands at 1601 and 1513 cm^{-1} were attribute of aromatic rings, according to vibrations of the aromatic skeleton. The bands at 1462 and 1424 cm^{-1} included a substantial contribution from the C-H bonds of the methyl groups (Tejado *et al.*, 2007). The band at 1328 cm^{-1} was observed for the syringyl units in lignin molecules, whereas guaiacyl units presented at 1266 cm^{-1}, according to the results of Popescu *et al.*, (2006) and Ibarra *et al.*, (2005). Raschip *et al.*, (2007) have presented evidence that lignin in wood and pulp consists of syringyl units with less guaiacyl units. The absorption bands at 1122 and 1032 cm^{-1} were attribute of secondary and primary hydroxyl groups, respectively. The band at 829 cm^{-1} was owing to aromatic CH out of plane vibration in a phydroxy phenylpropane unit of the syringyl units. The weak bands at 635 and 618 cm^{-1} were a characteristic of kraft lignin, which arise from C-S bonds. All of the FTIR experiments are consistent with previous researches (Tejado *et al.*, 2007, Nada *et al.*, 1998, El-Mansouri *et al.*, 2007, Garcia-González *et al.*, 2009, Yuan *et al.*, 2009, and Methacanon *et al.*, 2010).

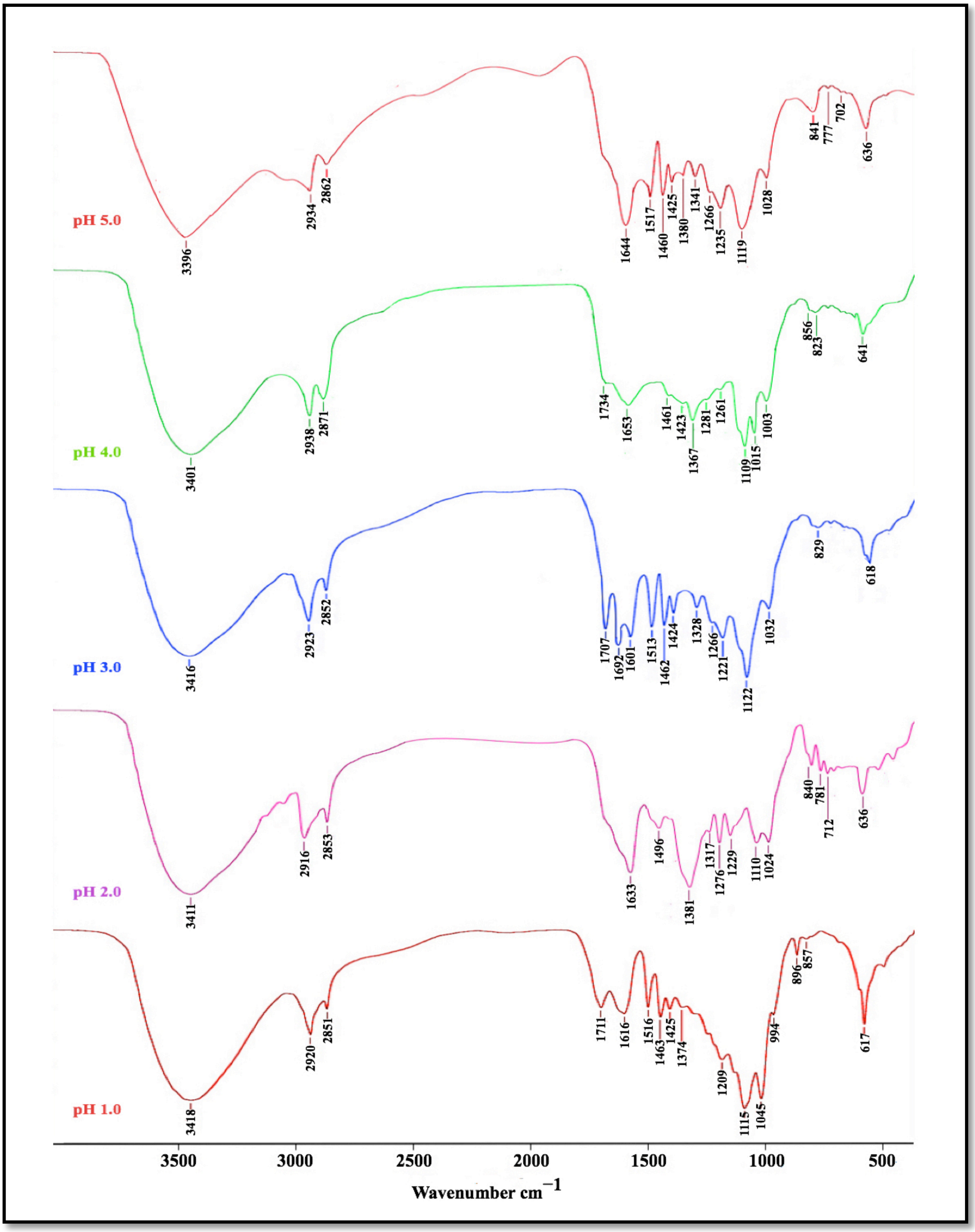


Figure 4.9 FTIR spectrums of the isolated lignin at pH 1-5.

Table 4.3 Assignment of FTIR absorption of the kraft lignin precipitated at pH 3.0.

Wavenumber (cm^{-1})			Assignment
pH3.0	**Previous work**		
	Nada *et al.*, 1998	**Methacanon *et al.*, 2010**	
3146	3440-3430	3390	OH stretching in phenolic and aliphatic structures
2923	2940-2930	2920	CH stretching in aromatic methoxyl or methylene groups of side chains
2852	2880-2689	2850	CH vibration of the -OCH_3 groups
1707	1727-1690	1710	C=O stretching (unconjugated C=O)
1692	-	1690	C=O stretching in conjugated p-substituted aryl ketones
1601, 1513	1690-1610, 1505	1605, 1515	Aromatic skeleton vibration
1462	1458	1460	C–H bending from methyl or methylene groups
1424	1425-1420	1425	CH asymmetric deformation of methyl group
1328	1370-1250	1330	Syringyl ring breathing with CO stretching vibrations (C–O stretching are those of the methoxyl and phenol groups)
1266	1260	1270	Guaiacyl ring breathing with CO stretch in lignin, CO linkage in guaiacyl aromatic methoxyl groups
1221	-	1220	C-O(H) stretching of phenolic OH and ether
1122	1160-1140	1155	OH stretching of secondary alcohol
1032	1044	1042	OH stretching of primary alcohol
829	844	832	Aromatic CH out of plane bending of Syringyl units
635, 618	630	630	CS bonds

TGA curves were studied and revealed the weight loss of substances in association with the temperature of thermal degradation. However, the first derivative curve shows the equal rate of weight loss. A thermal decomposition temperature being as a peak of this curve can be used to compare with the thermal stability characteristics of various materials. As shown in Table 4.4, the data from all samples of TGA showed the similar behavior of thermal degradation with T_d (decomposition temperature) in the range of 180 and 245°C. However, it showed nothing, among all samples. At pH 1.0, T_d of the kraft lignin precipitated was the lowest, showing the least thermal stability. On the other hand, the best thermal stability was at pH 3.0.

Table 4.4 Thermal properties of the kraft lignin precipitation.

Lignin	T_d (°C)	T_g (°C)
Precipitated at pH 1.0	210	106.12
Precipitated at pH 2.0	232	130.88
Precipitated at pH 3.0	245	131.81
Precipitated at pH 4.0	241	127.63
Precipitated at pH 5.0	237	128.41

The thermal stability seemed to be related to lignin molecular weight. It was increased with the molecular weight of lignin (Sun *et al.*, 2010). The temperature range of T_d of lignin has been operated in the range of 200 and 450°C, while hemicelluloses degenerated in the range of 160 to 300°C (Garcia et al., 2009, Fukushima *et al.*, 2015 and Sun *et al.*, 2010). Pyrolytic degradation of lignin affects fragmentation of inter-unit linkages, releasing monomeric phenol into a vapor phase. The breakage of methyl-aryl ether bonds was identified at below 400°C, but condensation or decomposition of aromatic rings occurred at 400-600°C. All lignin samples remained unvolatized due to the formation of highly condensed aromatic structure, after heating to 800°C (Tejado *et al.*, 2007 and Garcia *et al.*, 2009).

The glass transition temperature (T_g) values of the kraft lignin precipitation at pH 3.0 are shown in Figure 4.10 and Table 4.5. The results of this experiment correlated to their MW values, and corresponded to other studies that reported the T_g values of kraft lignin between 70 and 160°C (Tejado *et al.*, 2007, Trivedi *et al.*, 2014, and Garcia *et al.*, 2009).

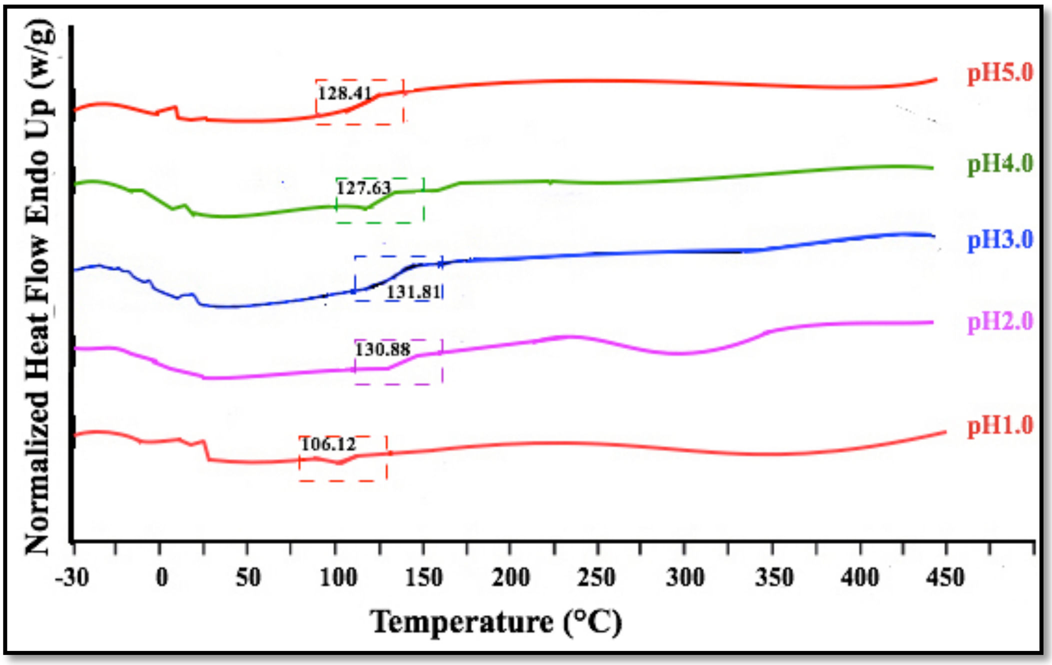


Figure 4.10 Differential scanning calorimetry (DSC) of the kraft lignin precipitated of all pH.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and the molecular weight distribution (polydispersity = M_w/M_n) of lignin obtained from the kraft lignin precipitation are listed in Table 4.5. They had relatively cramp molecular weight distribution (polydispersity values less than 2), which confirmed that they possessed a high fraction of low molecular weight (Methacanon *et al.*, 2010 and Kubo and Kadla, 2005).

Table 4.5 Molecular weight and molecular weight distribution of kraft lignin.

Lignin	Average MW (g mol^{-1})		Polydispersity
	M_w	M_n	M_w/M_n
Precipitated at pH 3.0 (This work)	1588	1082	1.47
Precipitated at pH 4.0 (Methacanon *et al.*, 2010)	1418	1071	1.32
Extract with dichloromethane (Methacanon *et al.*, 2010)	942	791	1.19
Hardwood kraft lignin (S. Kubo and J.F. Kadla, 2005)	2400	1263	1.90

The lignin recovery is not only impressive from an environmental standpoint alone but also with view economics as well. It can be reused for the acquisition of several chemical products, then the kraft lignin precipitated at pH 3.0 was selected for preparation of lignin-agarose hydrogel in the next step.

The reason that lignin at pH3 contributed the best yield and purity is probably due to its isoelectric value. Vishtal and Kraslawski (2011) describe that hemicellulose, especially xylan, can be dissolved in a suitable pH range. In general, cellulose is located within a lignin shell while the hemicellulose, with a random and amorphous structure, is located within the cellulose and between the cellulose and lignin. From a chemical perspective, hydrogen bonding exists between cellulose and lignin as well as cellulose and hemicellulose. Additionally, covalent linkages, mainly ether bonds, have been proposed to be present between cellulose and lignin (Zhang *et al.*, 2014). It depends on the raw materials, including the pulping conditions, and it is not necessary that all the pulp is always precipitated at this pH value. The hemicellulose was eliminated resulting in more purity of lignin.

Regarding the % yield, which is higher than the other pH, it may be that OPEFB lignin from kraft black liquor has an isoelectric value close to pH3. If the pH of the kraft black liquor is reduced to the isoelectric point, the lignin becomes more precipitated.

Dong *et al*. (1996), Yamaguchi *et al*., (2016), and Klapiszewski *et al*., (2013) reported that the isoelectric value of kraft lignin varies with the raw materials and kraft pulping condition.

4.3 Chemical characterization of lignin-agarose hydrogels

The lignin-agarose hydrogels were prepared in a various mixing ratio of lignin and agarose, containing epichlorohydrin as the cross-linking agent. The lignin-agarose hydrogels were cut into cylinders with a diameter of about an inch. The color of the lignin-agarose hydrogel depended on the amount of lignin content. The lignin solutions added to the agarose solutions decrease from 5%w/v (sample 1) to 1%w/v (sample 5). Sample 1 showed the dark brown color of lignin-agarose hydrogel. The color of sample 2, 3, 4, and 5 were gradually fades, respectively. It can be observed in Figure 4.10. The results showed that the addition of lignin solution caused increasing the color of hydrogel.

Figure 4.11 Color of lignin-agarose hydrogel with lignin from 5%w/v (hydrogel-1) to 1%w/v (hydrogel-5).

Epichlorohydrin (ECH) was added as a catalyzed cross-linking agent. It has generally been utilized for the cross-linking of carbohydrates in polysaccharide chemistry (Bai *et al.*, 2006, Chang *et al.*, 2008, Kubo and Kadla, 2005 and Denizli *et al.*, 2004). In alkaline conditions, the epoxy cycle from ECH opens and then binds to lignin with OH groups of ECH. After the chloride displacement, new epoxy groups can form, which react further with the hydroxyl groups from other lignin chains and thus the cross-linking between agarose and lignin occurs (Ciolacu *et al.*, 2012 and Denizli *et al.*, 2004), shown in Figure 4.11.

At high temperatures, the agarose molecules in the solution will behave in a random coil. In this phase, the molecular structure is independent and disorderly. As the temperature of the solution decreases, the double helices of each pair are brought together and bonded by hydrogen bonding.

The interaction of cross-linking could be related to two structural units that might or might not belonged to the similar agarose chain and might be accomplished without entanglement of the lignin. Also, others side interactions could occur. Instance, some ECH molecules might interact only with one hydroxyl group of agarose, but some ECH hydrolyzes do not interact with lignin. It was found that the ratio of lignin-agarose is an essential factor in the formation lignin-agarose network and also has an impact on the characteristics of the hydrogel, specifically on water retention capacitance (Bai *et al.*, 2006, Chang *et al.*, 2008, Ciolacu *et al.*, 2012 and Denizli *et al.*, 2004).

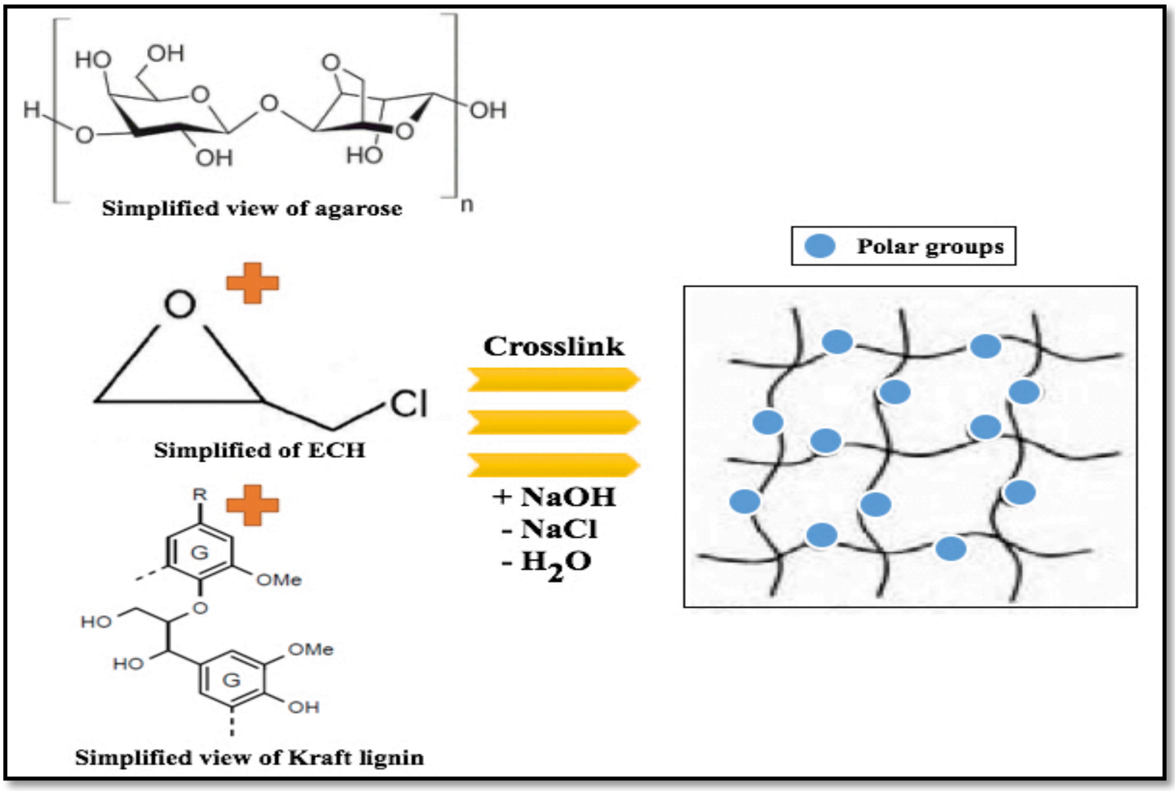


Figure 4.12 Schematic interaction of lignin–agarose hydrogels pathway using ECH as crosslinking agent.

The FTIR spectroscopy was used to verify the accomplishment of the cross-linking interaction between lignin and agarose. This was a very proficient analytical equipment to study the reactions in polymers. The interpolymer compatibility and the hydrogen bonding formation can be considered. The FTIR frequencies of hydrogel based on Lignin(L) and agarose(A) (A3L3, A3L3E10, and A5L3E10) are shown in Figure 4.12

FTIR bands of lignin-agarose hydrogels reflect the functional group of lignin interaction. FTIR spectra of the hydrogels were demonstrated in Table 4.6. The OH-stretching vibration was determined at the broad band between 3700 and 3000 cm^{-1}. The hydrogels spectra presented the strong wide band at 3353-3335 cm^{-1}, corresponding by the occurrence of phenolic and alcoholic hydroxyl groups related to hydrogen bonds. Conversely, the peak was stronger than the related peaks of lignin spectra (3416 cm^{-1}) but similar likewise to agarose spectra (3353 cm^{-1}). It indicated that the cross-linking interaction of lignin and agarose has occurred.

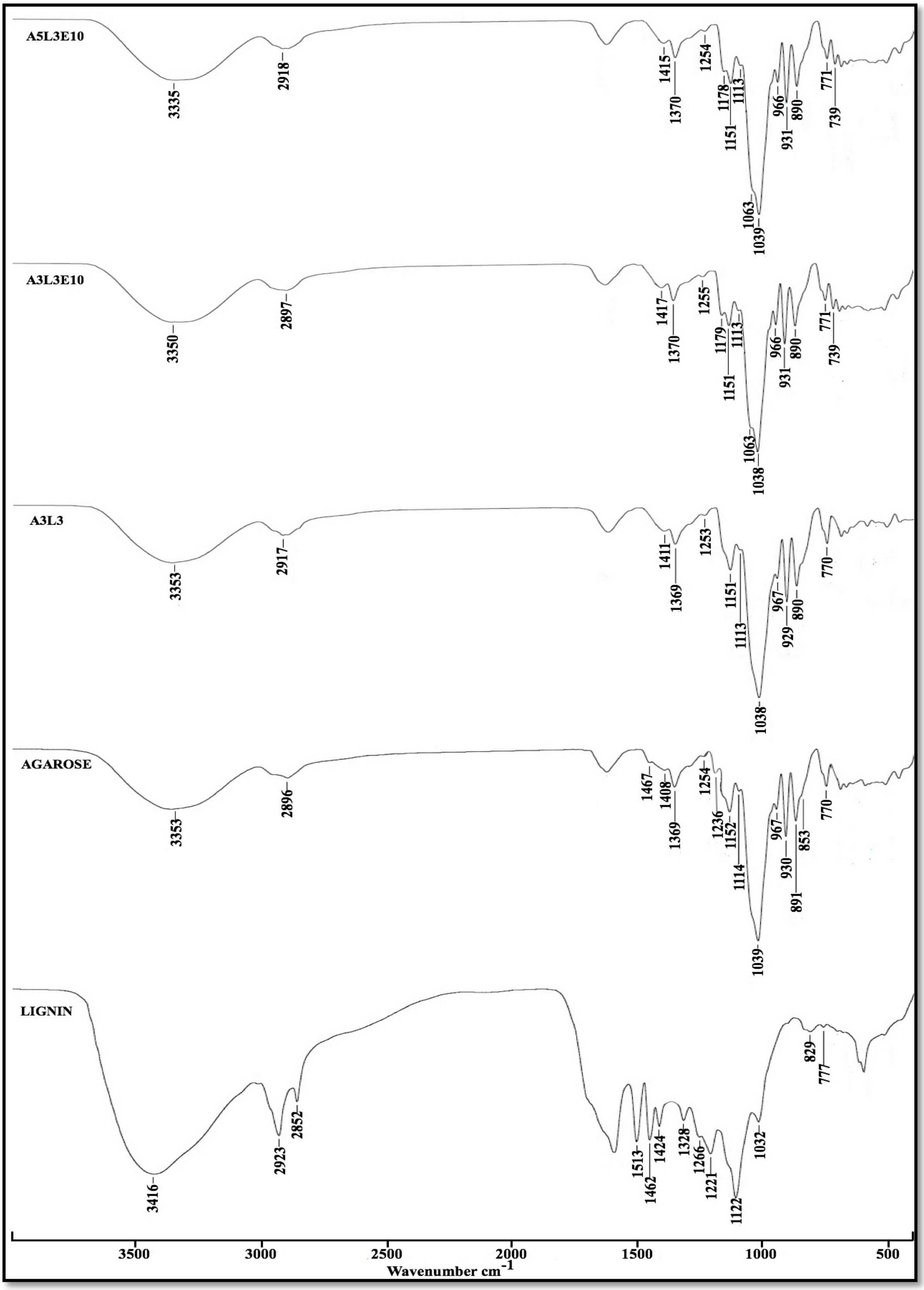


Figure 4.13 FTIR spectra of lignin (L), agarose (A), and hydrogel based on agarose and lignin (A3L3, A3L3E10, and A5L3E10).

Table 4.6 FTIR characteristics of samples obtained from the lignin and agarose hydrogels.

Hydrogel			Components	
A3L3	**A3L3E10**	**A5L3E10**	**Agarose**	**Lignin**
3353	3350	3335	3353	3416
2917	2897	2918	2896	2923
-	-	-	-	2852
1634	1639	1642	1637	1601
-	-	-	-	1513
-	-	-	1467	1462
1411	1417	1415	1408	1424
1369	1370	1370	1369	-
-	-	-	-	1328
1253	1255	1254	1254	1266
-	-	-	1236	1221
-	1179	1178	-	-
1151	1151	1151	1152	-
1113	1113	1113	1114	1122
-	1063	1063	-	-
1038	1038	1039	1039	1032
967	966	966	967	-
929	931	931	930	-
890	890	890	891	829
-	-	-	853	-
770	771	771	770	777
	739	739	-	-
714	715	715	714	722
692	692	692	691	-
665	665	665	666	-
-	-	-	-	635
611	-	-	617	618
579	-	-	559	-
534	537	537	537	537
483	487	485	484	-

The occurrence of the intensive band might observe the reformations of cross-linking between lignin and agarose at 2918-2877 cm^{-1} on the hydrogels spectra and corresponding to the C-H stretching vibration. This band was located at 2896 cm^{-1} from agarose spectra and was increased. The C-H stretching vibration of methoxyl group of lignin were assigned to 2918 and 2852 cm^{-1}. Also, the peak at 2918-2877 cm^{-1} region was observed for the lignin-agarose hydrogel spectra. It may have shifted from 2923 cm^{-1} which could reveal the appearance of lignin in the matrix of the hydrogel.

The stretching vibrations of carbonyl groups in lignin-agarose hydrogel were situated at 1650–1600 cm^{-1}. This may indicate the occurrence of lignin in the hydrogel. In term of lignin, the absorption bands located at 1642, 1639, and 1634 cm^{-1} were associated with ketone group at α-position and β-position. Also, the band at 1513 cm^{-1} of lignin spectra was associated with the vibration of aromatic rings that presented in the lignin, but this band absented in the spectra of the hydrogels. In case of agarose spectra, it appeared a peak determined to absorbed water, at 1637 cm^{-1} which were associated with the OH stretching (Sarkanen *et al.*, 1953 and Hergert and Kurth, 1967).

The intensive peak at 1462 cm^{-1} was specific to lignin spectra and was determined to deformative vibrations of CH_2 groups (Duri *et al.*, 1960). In agarose spectra, this band was preserved at the similar wavenumber. However, its intensity was recorded at 1467 cm^{-1}. The FTIR absorption band at 1408 cm^{-1} from agarose spectra, assigned to a symmetric CH_2 bending vibration, was shifted to a higher wavenumber, 1417-1411 cm^{-1} in the hydrogels spectra. This was because of the increasing of cross-linking interaction. This shift indicated the change of new intra- and inter-molecular hydrogen bonds (Chang *et al.*, 2008, Ciolacu *et al.*, 2012 and Socrates *et al.*, 2004). Furthermore, this band is the ‘crystallinity band’, and a reduction of its intensity reflects a decrease of the crystallinity of agarose. The band at 1369 cm^{-1} assigned as CH_2 bending, which, in the spectra of hydrogels, was shifted at 1370 cm^{-1} with an apparent increase in intensity.

The band at 1328 cm^{-1}, defined as C-OH bending in plane at C-3 or C-2, absented after cross-linking interaction, and the band at 1221 cm^{-1} that was assigned to CH_2 wagging, disappeared from the hydrogels spectra. Also, the band at 1236 cm^{-1} from agarose spectra, resulting to C-OH bending in plane at C-6, disappeared because of this cross-linking. The cross-linking interaction was the arrangement of ether bonds among lignin and agarose which were revealed in FTIR spectra of the hydrogels together with an enhance of aryl ether band (C-O-C stretching) at 1266-1253 cm^{-1} and of alkyl ether band at 1121-1113 cm^{-1} (C-O-C stretching) and 1063 cm^{-1} (C-O stretch from alkyl substituted ether). Duri *et al.*, (1960) and Raschip *et al.*, (2007) describe the band at 1063 cm^{-1} was caused by primary and the band at 1121-1113 cm^{-1} to deformation vibration of ether linkages and aliphatic ethers groups. The absorption band at 1266-1253 cm^{-1} was determined to asymmetric vibration of the C-O-C linkages in phenolic ether bonds.

In the spectra of lignin, the absorption band located at 1032 and 1122 cm^{-1} were the stretching vibrations of syringyl rings while the band at 1266 and 1221 cm^{-1} was instigated by stretching of C-H bonds in guaiacyl groups. The large band of alkyl ether groups correlated in the hydrogels spectra. Then, the absorption bands in the region 900–780 cm^{-1} of lignin spectra, caused by irregularity vibrations of C-H bonds on the benzene ring were found at 829 cm^{-1} and 777 cm^{-1} (Duri *et al.*, 1960 and Sarkanen *et al.*, 1953).

In agarose spectra, the absorption band at 853 cm^{-1} was assigned to C-O-C stretching at β-(1→4)-glycosidic linkages. FTIR spectra of the hydrogels with ECH did not reveal all these bands, however; a new band appeared at 739 cm^{-1}, assigned to the residual C-Cl stretching vibration (Raschip *et al.*, 2007 and Barrangou *et al.*, 2006). The vibration peaks of the acetal at 1179-1178 cm^{-1} of the hydrogel with ECH inferring that the chemical modifier reacted with the –OH of the agarose in the presence of the cross-linking agent (Barrangou *et al.*, 2006). The band with the greatest intensity from the spectra presented the same wavenumber (1179 cm^{-1} and 739 cm^{-1}) in FTIR spectra of hydrogels. The decrease of this band in the hydrogels with ECH spectra confirmed the occurrence of the cross-linking.

4.4 Physical characterization of lignin-agarose hydrogels

Gel strength of lignin-agarose hydrogel was characterized by texture personal analysis (TPA). It always use to determine the textural properties of foods. It is occasionally used in other industries, such as pharmaceuticals, gels, and personal care. Texture personal analysis shed light on the physical properties of the lignin-agarose hydrogel.

Table 4.7 showed the Texture personal analysis of lignin-agarose hydrogel. The best condition of lignin-agarose hydrogel was lignin 5%w/v, agarose 5%w/v, and ECH 10mL. The fracturability and hardness are about 76.989 gF and 181.491 gF, respectively. It contributed the best gel strength and good mechanical properties. In contrast, the lignin-agarose without ECH provided the lower mechanical properties when compared to the lignin-agarose with ECH. It had not showed the hardness property.

Table 4.7 Texture personal analysis of lignin-agarose hydrogel.

Sample	Fracturability (gF)	Hardness (gF)
Agarose 1%	16.734 ± 2.46	-
Agarose 3%	18.990 ± 5.14	-
Agarose 5%	26.024 ± 3.27	-
Agarose1%, Lignin1%	22.528 ± 0.49	-
Agarose1%, Lignin3%	21.407 ± 1.97	-
Agarose1%, Lignin5%	23.252 ± 0.43	-
Agarose3%, Lignin1%	27.346 ± 1.35	-
Agarose3%, Lignin3%	28.349 ± 3.70	-
Agarose3%, Lignin5%	27.528 ± 2.77	-
Agarose5%, Lignin1%	30.715 ± 4.59	-
Agarose5%, Lignin3%	33.160 ± 2.22	-
Agarose5%, Lignin5%	31.685 ± 2.81	-
Agarose1%, Lignin1%, ECH5mL	25.182 ± 0.86	28.134 ± 1.88
Agarose1%, Lignin3%, ECH5mL	25.995 ± 1.78	30.103 ± 1.15
Agarose1%, Lignin5%, ECH5mL	27.074 ± 2.77	32.541 ± 1.34
Agarose3%, Lignin1%, ECH5mL	34.326 ± 0.43	39.263 ± 2.10
Agarose3%, Lignin3%, ECH5mL	34.148 ± 1.46	39.721 ± 3.93
Agarose3%, Lignin5%, ECH5mL	35.964 ± 0.67	42.469 ± 3.01
Agarose5%, Lignin1%, ECH5mL	49.692 ± 1.69	52.719 ± 1.73
Agarose5%, Lignin3%, ECH5mL	47.498 ± 0.82	57.272 ± 3.74
Agarose5%, Lignin5%, ECH5mL	48.873 ± 0.75	56.453 ± 3.93
Agarose1%, Lignin1%, ECH10mL	31.576 ± 1.70	58.576 ± 5.05
Agarose1%, Lignin3%, ECH10mL	32.109 ± 0.79	62.930 ± 2.88
Agarose1%, Lignin5%, ECH10mL	30.186 ± 1.48	62.187 ± 5.53
Agarose3%, Lignin1%, ECH10mL	47.057 ± 0.35	109.501 ± 6.12
Agarose3%, Lignin3%, ECH10mL	48.018 ± 0.83	154.426 ± 5.86
Agarose3%, Lignin5%, ECH10mL	48.423 ± 1.96	158.469 ± 6.26
Agarose5%, Lignin1%, ECH10mL	71.863 ± 2.67	169.571 ± 1.71
Agarose5%, Lignin3%, ECH10mL	74.670 ± 3.20	176.222 ± 5.57
Agarose5%, Lignin5%, ECH10mL	76.989 ± 2.82	181.491 ± 5.59

The fracturability, hardness and springiness of lignin-agarose hydrogel were shown in Figure 4.13. Fracture stress value was highly correlated with hydrogel firmness or hardness. It depended on the concentration of hydrogel composition. The fracturability increased with the increase of the lignin, agarose and ECH concentration. Additionally, compressing force or hardness was defined as compressed or uncompressed sample deforms before breaking (Ciolacu *et al.*, 2012).

Both fracturability and hardness were corresponding to the deformability of lignin-agarose hydrogel. On the other hand, springiness value indicated the elastic or completely recoverable after deformation of the hydrogel to about 10%. However, all fracturability, hardness, and springiness were also correlated to the sensory evaluation.

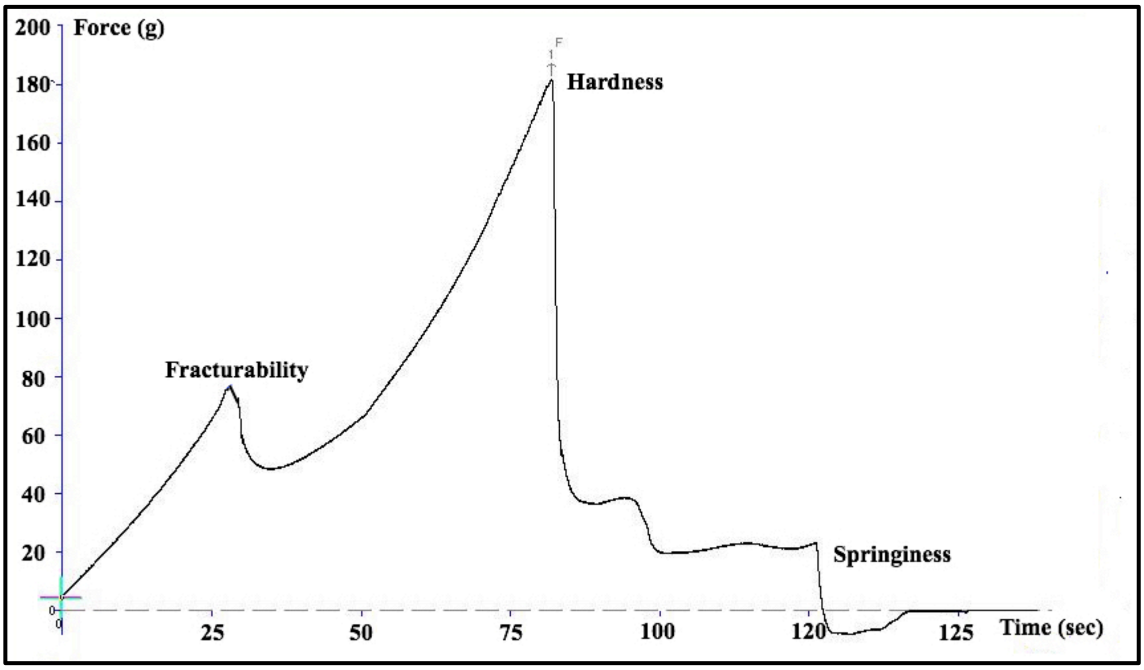


Figure 4.14 Fracturability, ideal hardness, and springiness of the lignin-agarose hydrogel (agarose5%, Lignin5%, ECH10mL).

4.5 Chemical characterization of lignin-xanthan hydrogels

Lignin is a complex polymer that is clearly visible with the FTIR spectrum. The overlapping bands of partial absorption of functional groups are common.

The FTIR spectra of the xanthan/lignin (XL) hydrogels with and without the crosslinking agent were investigated. FTIR characteristics of xanthan/lignin (XL) and xanthan/lignin with ECH (XL-ECH) are presented in Table 4.8 and Figure 4.14.

Table 4.8 FTIR characteristics of samples obtained from the lignin and xanthan hydrogels.

Hydrogel		**Components**	
XL	**XLE**	**Xanthan**	**Lignin**
3340	3300	3428	3416
2921	2919	2918	2923
-	-	2853	2852
1718	1725	1731	-
1603	1602	1621	1601
-	1512	-	1513
-	-	-	1462
1410	1409	1415	1424
1372	1370	1374	-
-	1332	-	1328
1238	1240	1275	1266
-	-	-	1221
-	1193	-	-
1156	1154	1160	-
-	-	-	1122
1030	1025	1064	1032
893	895	893	-
793	793	793	-
-	740	775	777

The spectrum of lignin was presented into two major regions. The bands in the 3550-2700 cm^{-1} range defined to the –OH groups of the bonded in aliphatic and aromatic groups, e.g. the methyl groups. In the lignin spectrum, the absorption band centered at 3380 cm^{-1} has a similar shape of the lignin gained from OPEFB and the peak varies in the closed limits between 3416-3400 cm^{-1}. For this latter lignins, the position of the peak was shifted to higher wavelength, which means the better interactions of water absorbed by the lignin molecules.

However, the region at 3600-2700 cm^{-1}, the absorption band around 3416 cm^{-1} meant to the vibration of the –OH groups. They have approximately the similar shape as for the samples obtained by mixing of the xanthan and lignin. The major bands of the hydrogels FTIR spectra are demonstrated in Table 4.10.

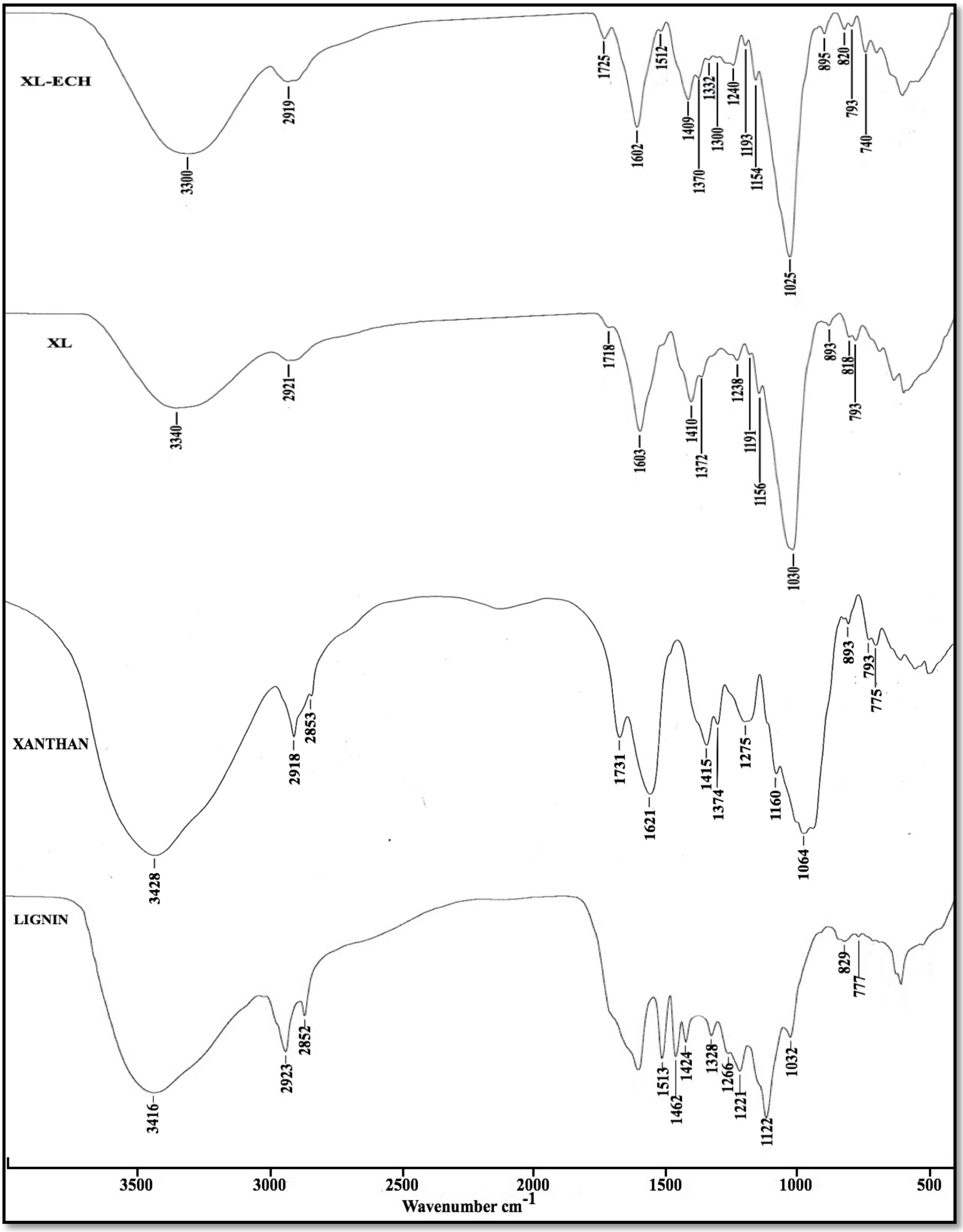


Figure 4.15 FTIR spectra of lignin-xathan hydrogel based on xanthan with and without ECH.

Table 4.9 Assignment of FTIR absorption of the xanthan/lignin hydrogels.

Wavenumber (cm^{-1})	Assignment
3380–3300	Hydroxyl groups in phenolic and aliphatic structures
2930–2910	CH stretching in aromatic methoxyl or methylene groups of side chains
1740–1715	C=O stretching (unconjugated C=O)
1690–1600	Aromatic skeleton vibration
1620	–C=O of pyruvate
1515–1505	C=C stretching of the aromatic ring (G)CH deformation
1460–1370	Asymmetric C–H bending from methoxyl groups
1430–1410	C–H asymmetric deformation in $–OCH_3$
1300–1200	Aromatic C–O stretching vibrations (C–O stretching are those of the methoxyl and phenol groups)
1266	Guaiacyl ring breathing, C–O stretch in lignin, C–O linkage in guaiacyl aromatic methoxyl groups
1128–1110	Aromatic C–H in plane deformation (typical for S units) plus OH stretching of secondary alcohol
1060-1020	OH stretching of primary alcohol (C–H in plane deformation of G ring)
892	C_1–H of b-pyranose
830–815	C–H out of plane in position 2 and 6 of S units

The FTIR absorption of the xanthan/lignin hydrogels are presented in Table 4.10. Modification epichlorohydrin (ECH) has not presented a new absorbance. In particular, the characteristic peaks of the C–Cl bond (740 cm^{-1}) are not present in the XL hydrogel but appear in the FTIR spectrum of the XL-ECH hydrogel. The modification of ECH hardly influenced the peak of the amide I (1720–1520 cm^{-1}) and amide II absorption (1480–1360 cm^{-1}), although will cause in the spectrum of the amide III region (1370–1150 cm^{-1}). This is characteristic of the XL-ECH hydrogel samples.

Faria *et al.*, (2011) and Raschip *et al.*, (2012) described the absorbance of intermolecular bands within xanthan gum. The band of OH and NH were found at 3427 cm^{-1} and CH, COOH, and C=O were associated with 2920, 1729, and 1618 cm^{-1}, respectively. Xanthan gums showed the higher intensity at 1406 and 1050 cm^{-1} due to O–H and C–H bending vibrations, respectively. In the FTIR spectrum of the hydrogels, all bands were broader to prove that crosslinking occurs.

In comparison with the band for xanthan gum assigned to –OH (3427 cm^{-1}), the spectrum bands of the XL and XL-ECH hydrogels were shifted to the bottom wave number at 3340 and 3300 cm^{-1}, respectively. It shows that the interaction between molecules with hydrogen bonds occurs in the studied samples.

The intensities of the acetal C–O peak at 1193 cm^{-1} of the XL-ECH hydrogel samples were stronger than the bands of xanthan gum at 1157 cm^{-1}. This implies that chemical reactions with -OH of xanthan gum in the presence of a crosslinking agent.

4.6 Physical characterization of lignin-xanthan hydrogels

Xanthan is generally considered non-gelling polymer , but it can be used as both chemical and physical components (Vilgis, 2005, Desbrieres *et al.*, 2009). In this study the xanthan and lignin mixture in the presence of ECH contributed the higher viscosity comparing to the mixture without crosslinking agent. However, they could not form the solid gel similar to agarose-lignin hydrogel. The hair gel of xanthan gum is shown in Figure 4.15.

Figure 4.16 Xanthan hydrogel without lignin.

The influence of ECH on the viscosity of xanthan/lignin hydrogels were shown in Table 4.9. The viscosity of lignin-xanthan hydrogel depended on the crosslinking agent addition. The viscosity increased with the addition of ECH. The viscosity of XL-ECH hydrogel was higher than the XL hydrogel approximately 16×10^3 cP and 17×10^3 cP for both spindle no.06 and no.63, respectively. It is hypothesized that the ion bridge occurs when either an inter- or intra-molecular ionic "crosslink" is formed. The crosslink between ECH and polymer chains would introduce a stronger network. It resulted to have higher viscosity.

Table 4.10 Influence of ECH on xanthan/lignin hydrogel rheology.

Sample	Viscosity (%Touque)	
	Spindle No.06 (0.5 rpm)	Spindle No.63 (0.5 rpm)
Xanthan	153×10^3 cP	148×10^3 cP
XL	160×10^3 cP	154×10^3 cP
XL-ECH	176×10^3 cP	171×10^3 cP

4.7 Density and porosity of gum-lignin aerogels

The lignin-based hydrogel was converted into aerogel by drying method. Liquids in hydrogel structure are replaced by hydrogen gas in a stable network with little or no shrinkage and the dried hydrogels have a very high porosity. Aerogel was firstly achieved under supercritical conditions but it is now possible under ambient drying conditions as well (Grishchenko *et al.*, 2013a). In addition, the trade name of products developed by hydrogel that was dehydrated with freeze drying is cryrogels.

This study investigated the effects of agarose, lignin, and ECH concentrations on the texture properties of aerogels. All of the agarose-lignin aerogels showed that the bulk density was in the range of 0.80–2.20 g/cm^3. The aerogels have a porous structure with low density (as low as 0.808 g/cm^3) which is measured as the ratio between the mass of the aerogel and its volume. Conversion of hydrogel to aerogels has a certain degree of shrinkage. The overall shrinkage caused by solvent exchange and drying methods (Freeze drying, FD and Supercritical drying, CPD) in the range from 6.5 to 34.1% in all samples. Despite the shrinkage, the aerogels still the original shape and have a relatively high surface area in the range of 0.60–1.25 m^2/g for freeze drying aerogels. However, the aerogels made by supercritical drying will have a specific surface area between 1.21 - 2.44 m^2/g.

The pore size of lignin-based aerogel measured by BJH method was about 16.01-25.40 Å. Our result was good agreement with previously reported such as Sehaqui *et al.* (2010). The result of a specific surface area of 1.5–4.5 m^2/g for CNF aerogels was measured at the density ranging from 0.7 to 10.3 g/cm^3.

The amount of crosslinking agent that causes an increase in surface area but it also decreased the average pore diameter, as shown in Table 4.11. The concentration of lignin has little influence on the surface area and the average pore diameter. The amount of ECH may be a great feature for texture of aerogel (high surface area, adsorption average pore diameter).

Table 4.11 List of textural properties of aerogels.

Sample Name	**Volume (cm^3)**	**Bulk density (g/cm^3)**	**BET Surface area (m^2/g)**	**Adsorption average pore diameter (Å)**
XL-ECH - FD	0.2102 ± 0.0006	1.6571 ± 0.0051	0.0737	24.5164
A3 - FD	0.0824 ± 0.0011	1.8435 ± 0.0449	0.6081	18.3015
A3 - CPD	0.0982 ± 0.0046	1.3514 ± 0.0101	1.2117	17.0288
A1L3E5 - FD	0.0909 ± 0.0013	2.0952 ± 0.0796	1.1982	24.3330
A1L3E5 - CPD	0.1014 ± 0.0021	1.0402 ± 0.0049	1.7581	17.4415
A3L3 - FD	0.0848 ± 0.0005	2.1902 ± 0.0284	0.8612	22.8540
A3L3 - CPD	0.0989 ± 0.0006	0.9952 ± 0.0016	1.3002	18.1176
A1L3E10 - FD	0.0965 ± 0.0024	1.6480 ± 0.0596	1.2132	24.5781
A1L3E10 - CPD	0.1008 ± 0.0005	0.8972 ± 0.0084	1.9832	18.5068
A3L3E10 - FD	0.0878 ± 0.0019	1.5571 ± 0.0305	1.1874	24.2856
A3L3E10 - CPD	0.1169 ± 0.0081	0.8657 ± 0.0015	2.1982	16.0157
A5L5E10 - FD	0.0909 ± 0.0010	1.6571 ± 0.0115	1.2453	25.4045
A5L5E10 - CPD	0.1115 ± 0.0104	0.8084 ± 0.0546	2.4341	16.4934

4.8 Morphology of gum-lignin aerogels

The SEM micrographs of aerogels obtained from agarose, xanthan-lignin with ECH (XL-ECH), agarose-lignin (AL) and agarose-lignin with ECH (ALE) are presented in Figure 4.16 and Figure 4.17. The cross-section of the lignin based aerogels indicated a nanoporous structure with the pore sizes between 16.01 Å (A3L3E10-CPD) and 26.40 Å (A5L5E10 - FD), shown in Table 4.11. It has been observed that the average pore size of the aerogels increased slightly with increasing the lignin content, which suggests that a higher water absroption could be achieved. This hypothesis is a good agreement with the data obtained from Ciolacu *et al.*, (2012).

In addition, the structure of aerogels has also been greatly influenced by the content of lignin and ECH, thus leading to a more homogenous and less dense structure (Ciolacu *et al.*, 2012, and Thakur *et al.*, 2014). The amount of ECH could reduce the shrinkage of samples. Navarra et al. (2015) have described that it may involve the chemical crosslinking between OH group of lignin and ether-based linkage of ECH. It can be concluded that the hydrogels have been expected to be crosslinked chemically and physically. However, it was found that the aerogels made from freeze drying (FD) had the porosity less than the aerogels made from supercritical drying (CPD).

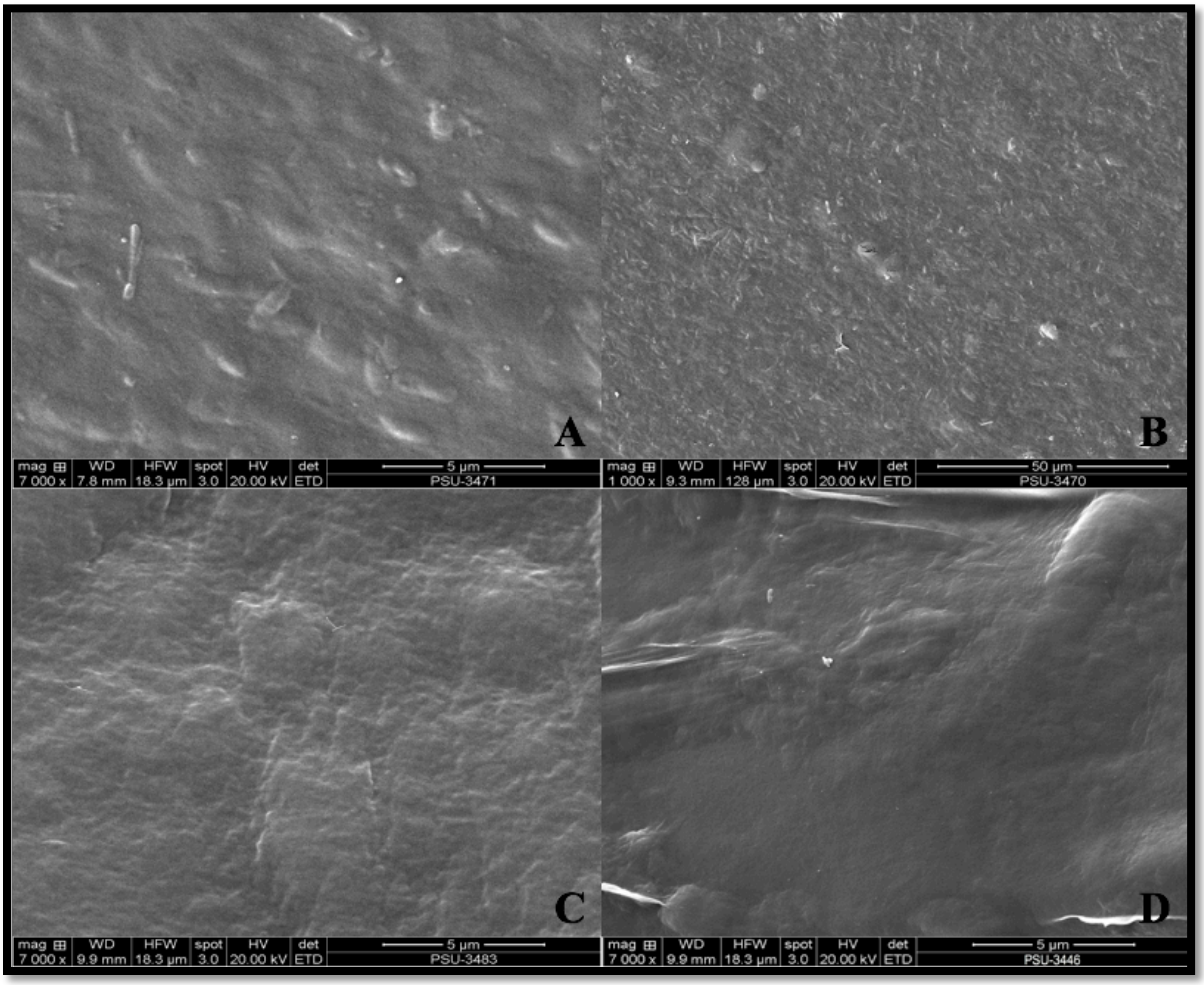


Figure 4.17 SEM images of the surface of aerogel XL-ECH-FD (A and B), A3-FD (C), and A3-CPD (D).

It is noteworthy that the surface of the aerogels made from freeze drying are denser and smoother than the aerogels made from supercritical drying, compared to the same condition and almost equal volume of the aerogels. The aerogels made from freeze drying have a density of 1.55-2.19 g/cm^3 while the aerogels made from supercritical drying have a density of 0.80-1.65 g/cm^3. On the other hand, the pore sizes of the aerogels made from supercritical drying smaller than the aerogels made from freeze drying. The aerogels made from supercritical drying have the pore sizes between 16.01-18.50 Å (1.60-1.85nm) while the aerogels made from freeze drying contributed the pore sizes between

18.30-25.40 Å (1.83-2.54nm). In addition, the bulk density and pore sizes of XL-ECH were 0.073 g/cm^3 and 24.52 Å (2.45nm), respectively.

This suggests that the drying process of aerogel has effected to the appearance of pore in aerogel. For freeze drying process, water molecules were evaporated from inside to the surface during drying of the aerogels, then resulting to a lower porosity inside the aerogels than the surface and make a higher density inside the aerogels than the surface. The density of aerogel depended on the thickness of the sample size because the shrinkage of the aerogel increases during the drying process.

The shrinkage rate of aerogels made from supercritical drying (CPD) was less than 20% but the aerogels obtained from freeze drying (FD) was over 30%. The results demonstrate that the volumetric shrinkage depended the drying process of aerogels. Supercritical drying (CPD) has the lower shrinkage when compared to the freeze drying process (FD) when the initial volume was 0.125 cm^3. This is consistent with the results of other researchers (Kim *et al.*, 2005, and Błaszczyński *et al.*, 2013). Shen *et al.*, (2016) described the slow evaporation of water during aerogel forming resulted to decrease the cavernous structure and a smoother surface.

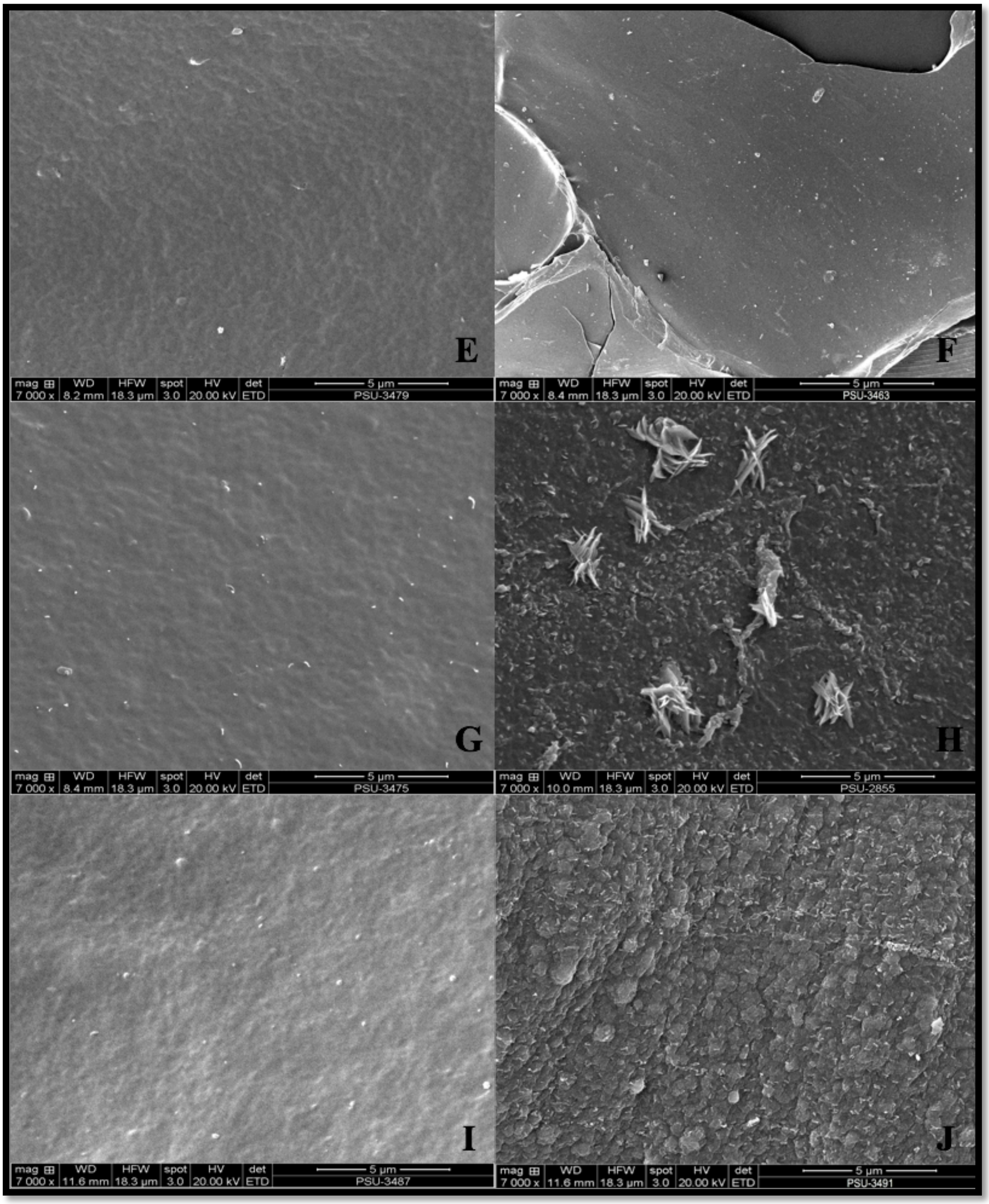
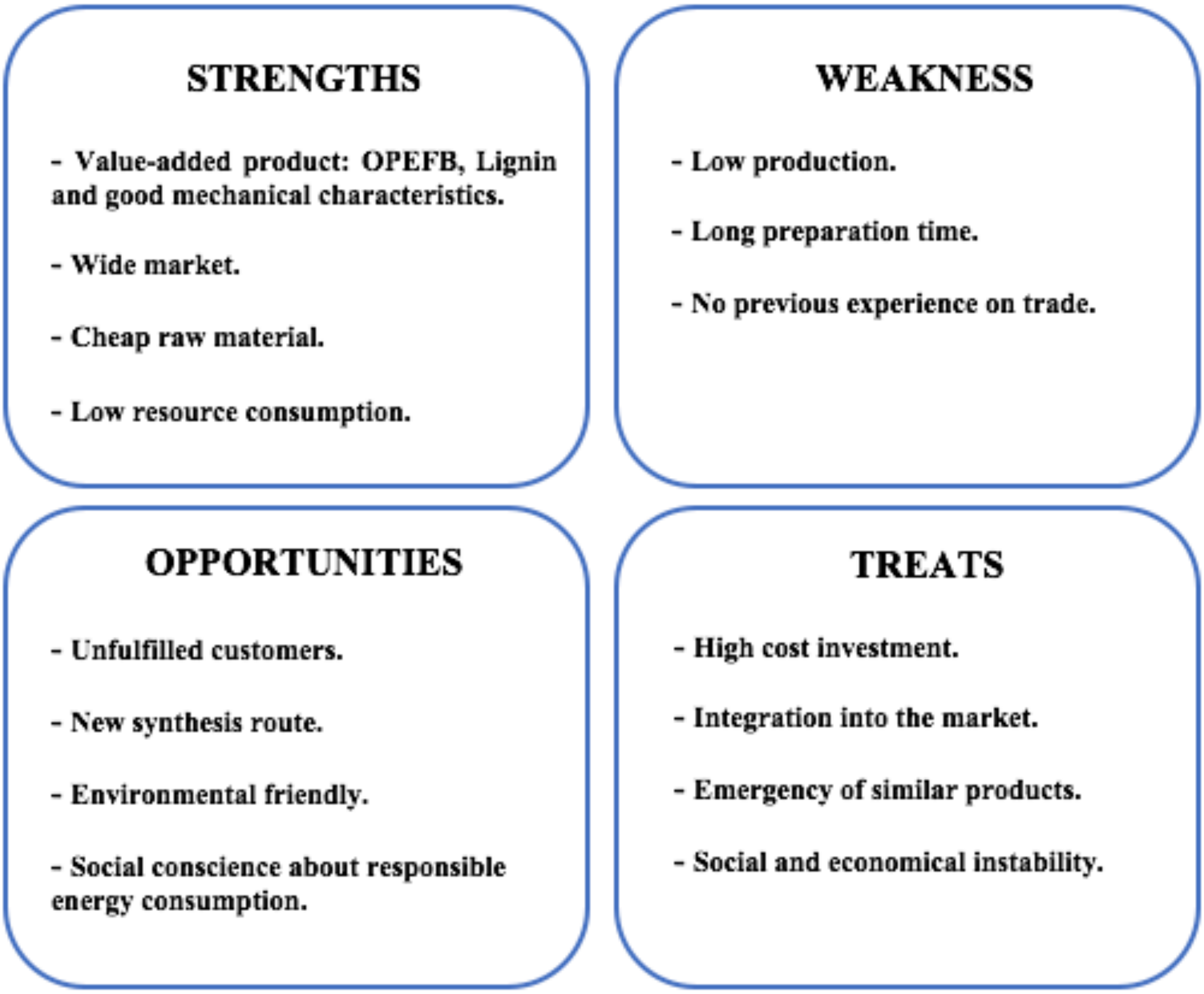


Figure 4.18 SEM images of the surface A3L3-FD (E), A3L3-CPD (F), A1L3E5-FD (G), A1L3E5-CPD (H), A5L5E10-FD (I) and A5L5E10-CPD (J).

4.9 Analyze the strengths and weaknesses of agarose-lignin aerogel

The SWOT matrix concerning the agarose-lignin aerogels is shown in Figure 4.18. Strengths, weaknesses, threats and opportunities faced by most relevant processes will appear in the list. It is important to mention that the SWOT matrix is just a tool and must be based on a broad knowledge of the current situation and future trends of the market (Fernández-Ronco *et al*., 2013 and Haghgoo *et al*., 2002).



STRENGTHS

- Value-added product: OPEFB, Lignin and good mechanical characteristics.
- Wide market.
- Cheap raw material.
- Low resource consumption.

WEAKNESS

- Low production.
- Long preparation time.
- No previous experience on trade.

OPPORTUNITIES

- Unfulfilled customers.
- New synthesis route.
- Environmental friendly.
- Social conscience about responsible energy consumption.

TREATS

- High cost investment.
- Integration into the market.
- Emergency of similar products.
- Social and economical instability.

Figure 4.19 SWOT matrix for the production of agarose-lignin aerogels.

According to the SWOT matrix is some threats such as the high investment needed for the primary material (agarose), there are similar products potentially qualify better and cheaper and the difficulty of bringing the product into the market. There are also many other weaknesses, one of the weakness is the lignin extracted with a minimum amount. Consequently, it takes longer to obtain lignin, which is sufficient to be used in other analytical procedures. However, one of the strengths is the added value of the byproduct from pulp and paper industry. In this study, investment analysis is based on production in the laboratory.

Considering that in the laboratory scale production, the production of agarose-lignin aerogel in the laboratory scale is limited to 1 liter per batch. Table 4.12 shows the quantity of raw materials, prices and suppliers required to make the agarose-lignin aerogels per batch. The agarose is the most expensive material, followed by the ECH using as the crosslinking agent. The total cost of the production agarose-lignin aerogels is about 6,110 Baht/batch (excluded the total cost of the equipment and the cost of the drying process). As mentioned above, investments are calculated based on laboratory scale (Fernández-Ronco *et al.*, 2013 and Haghgoo *et al.*, 2002).

Table 4.12 The raw materials, prices and suppliers to obtain the agarose-lignin aerogels per batch.

Raw materials	Mass	Price (Baht)	Supplier
Agarose	0.1 kg.	3,350	Gibthai Co., Ltd
ECH	500 mL.	2,760	Sigma–Aldrich
Total		6,110	

There are many studies the synthesis of aerogels using supercritical drying (Mutalik *et al.*, 2013). However, the products of these processes are some disadvantage when compared with those obtained from the freeze drying. For example, the more complicated method, the demand of expensive raw materials and the consumption of large amounts of energy and CO_2.

The data for this research leads to further study in the future. The recommendation for changing in this research is to change raw materials in which cheaper than before with similar properties. It can reduce the cost of aerogel and it be able to compete with aerogel in the market.

CHAPTER 5

GENERAL CONCLUSIONS

The mechanical properties of pulp sheets obtained from the kraft process, such as the ring crush index (RCI), tensile index (TI), and bursting index (BI), are higher than that of pulp sheets obtained from the soda process. Due to the higher delignification of kraft pulping process, the mechanical properties of its pulp were higher than soda pulp. The amounts of residual lignin in soda pulp led to prohibit the fiber network of fibrous material and decreased the strength of pulp sheets. In the kraft pulping process, lignin has been dissolved in large quantities of black liquor. They were successfully separated from the black liquor by sulfuric acidic at pH 6. The yield of isolated lignin was about 16 - 25 % of the initial wood mass.

The optimal condition of lignin separation from kraft black liquor was studied by acidic process. OPEFBs lignin was obtained by precipitation at pH 4, 3, and 2. The percent yield of isolated lignin obtained from the soda process was lower than the kraft process around 50-60%. It was due to the chemical reaction of kraft pulping at high pressure and temperature. Moreover, the COD of kraft black liquor tended to decrease with decreasing the lignin content in black liquor. Effect of pH on the reduction of COD in wastewater was observed to be noteworthy and also showed a tendency to decrease the color of wastewater after lignin separation.

The precipitated pH and composition of the raw materials have influenced on the recovery of OPEFBs lignin from black liquor. The isolated lignin from the OPEFBs kraft black liquor showed greater intensity at pH 3.0. It contributed the highest yield and purity while the lignin precipitation at pH 2.0 and pH 1.0 contributed the lowest lignin yield and purities, respectively. However, altering the pH of lignin precipitation has never affected to the chemical component of recovered lignin.

The chemical composition of all isolated lignin samples were verified by FTIR analysis. TGA curves of thermal degradation of recovery lignin were studied and revealed that the best thermal stability was the lignin precipitated at pH 3. The glass transition temperature (T_g) value of the kraft lignin precipitation at pH 3.0 was the highest. It can be concluded that OPEFBs lignin obtained by precipitation at pH 3 has a potential to be used as a raw material of lignin based hydrogel and aerogel.

The lignin-agarose hydrogels were prepared in a various mixing ratio of lignin and agarose, containing epichlorohydrin as the cross-linking agent. FTIR spectroscopy has verified the accomplishment of the chemical interaction among lignin, agarose and cross-linking agent, ECH. The color of the lignin-agarose hydrogel also depended on the amount of lignin content.

Gel strength of lignin-agarose hydrogel was characterized by texture personal analysis (TPA). The best condition of lignin-agarose hydrogel was lignin 5%w/v, agarose 5%w/v, and ECH 10mL. The lignin-agarose without ECH provided the lower mechanical properties when compared to the lignin-agarose with ECH.

Hydrogel based on lignin and xanthan gum was prepared by using epichlorohydrin as the crosslinking agent. The chemical characterization of the xanthan/lignin (XL) and xanthan/lignin with ECH (XL-ECH) were described by FTIR analysis. The interactions of crosslinked structures of the hydrogel were observed. They have affected to the appearance properties of the lignin-xanthan hydrogel. It is the cause of higher viscosity of lignin based hydrogel. ECH addition achieved an increase in viscosity of lignin-xanthan hydrogel.

Aerogels can be prepared by freeze drying and supercritical drying process. The lignin-agarose aerogel obtained from supercritical drying process showed a special porosity with low density. The amount of crosslinking agent was not only increasing the surface area but also reducing the adsorption average pore diameter. On the other hand, the lignin dosages have not influenced on the surface area and pore size diameter. The shrinkage of aerogels was decrease with ECH addition. It was due to the polymer network among lignin, gum and crosslinking agent, ECH. The volumetric shrinkages of lignin based aerogels obtained from supercritical drying were lower than aerogels obtained from freeze drying. However, the aerogels obtained from both methods exhibited good homogeneity, surface area, porosity and apparent density. Moreover, they are the nanoporous materials.

According to the SWOT matrix, the important strength of lignin-based aerogel is the added value from the by-product of pulp and paper industries while the main threats is the higher cost of raw material and drying process. However, the results demonstrated that lignin-agarose hydrogel might offer a significant possibility to tissue engineering applications, biomedical, biodegradability, and medication conveyance. It has given for a point of view with respect to further possible developments.

REFERENCES

Akdeniz, N., Sahin, S., and Sumnu, G. 2006. Functionality of batters containing different gums for deep-fat frying of carrot slices. Journal of Food Engineering. 75. pp. 522-526.

Alén, R., Mân Vu, T.P., and Pakkanen, H. 2003. Delignification of bamboo (Bambusa procera acher): part 1. Kraft pulping and the subsequent oxygen delignification to pulp with a low kappa number. Industrial Crops and Products. 19(1). pp. 47–57.

Amaral-Labat, A., Szczurek, A., Fierro, V., Pizzi, A., Stein, N., Boulanger, C., and Celzard, A. 2010. Pore structure and electrochemical performances of tannin-based carbon cryogels. Biomass and Bioenergy. 39. pp. 274-282.

Anttila, M., Kataja, K., and Kela, L. 2012. The self-organization of starch on paper. Nordic Pulp and Paper Research Journal. 27. pp. 621–630.

Ashley, C.S., Hostetler, J.L., Stewart, D., Daitch, C.E, and Norris, P.M. 2001. Optical polarized reflectance characterization of thin aerogel and xerogel films. Journal of Non-Crystalline Solids. 225. pp. 19-23.

Astimar, A.A., Mohamad, H., and Anis, M. 2002. Preparation of cellulose from oil palm empty fruit bunches via ethanol digestion: Effect of acid and alkali catalysts. Journal of Oil Palm Research. 14(1). pp. 9-14.

Araújo, M., Gonçalves, P., Benevenuto, F., and Cha, M.Y. 2013. Comparing and combining sentiment analysis methods. COSN'13 Proceedings of the first ACM conference on Online social networks. Boston, Massachusetts, USA. October 07 – 08.

Bai, Y.X., and Li, Y.F. 2006. Preparation and Characterization of Cross Linked Porous Cellulose Beads, Carbohydrate Polymer. 64. pp. 402–407.

Barrangou, L.M., Daubert, C.R., and Foegeding, E.A. 2006. Textural properties of agarose gels. II. Relationships between rheological properties and sensory texture, Food Hydrocolloids. 20. pp. 184-195.

Berg, M.N., and Pickering, T. 2007. Biodegradation of lignin and hemicelluloses. In Biochemistry of Microbial Degradation, C. Ratledge, editor. Kluwer Academic Publishers, Dordrecht, U.S.A., pp. 233-277.

Bhardwaj, Y.K., Biswal, J., Kumar, V., Goel, N.K., Dubey, K.A., Chaudhari, C.V., and Sabharwal, S. 2007. Radiation-induced grafting of acrylamide onto guar gum in aqueous medium: Synthesis and characterization of grafted polymer guar-g-acrylamide. Radiation Physics and Chemistry. 76(10). pp. 1624-1630.

Błaszczyński, T., Ślosarczyk, A., and Morawski, M. 2013. Synthesis of Silica Aerogel by Supercritical Drying Method. Procedia Engineering. 57. pp. 200-206.

Boerjan, W., Ralph, J., and Baucher, M. 2003. Lignin biosynthesis. Annual Review of Plant Biology. 54(1). pp. 519-546.

Braghiroli, F.L., Fierro, V., Izquierdo, M.T., Parmentier, J., Pizzi, A., and Celzard, A. 2014. Kinetics of the hydrothermal treatment of tannin for producing carbonaceous microspheres. Bioresource Technology. 151. pp. 271-277.

Brodin, I., Sjöholm, E., and Gellerstedt, G. 2010. The behavior of kraft lignin during thermal treatment. Journal of Analytical and Applied Pyrolysis. 87. pp. 70-77.

Cao, Z., Gilbert, R. J., and He, W. 2009. Simple agarose–chitosan gel composite systemfor enhanced neuronal growth in three dimensions. Biomacromolecules. 10(10). pp. 2954–2959.

Carrasco-Marin, F., Fairén-Jiménez, D., and Moreno-Castilla, C. 2009. Carbon aerogels from gallic acid–resorcinol mixtures as adsorbents of benzene, toluene and xylenes from dry and wet air under dynamic conditions. Carbon. 47(2). pp. 463-469.

Çetin, N., and Özmen, N. 2002. Use of organosolv lignin in phenol–formaldehyde resins for particleboard production: I. Organosolv lignin modified resins. International Journal of Adhesion and Adhesives. 22(6). pp. 477-480.

Chen, Y., and Li, P. 2010. Fabrication of High-Concentration and Stable Aqueous Suspensions of Graphene Nanosheets by Noncovalent Functionalization with Lignin and Cellulose Derivatives. The Journal of Physical Chemistry. 114(9). pp. 3811-3816.

Chen, X., Liu, L., and Mao, S. 2011. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. Science. 331. pp. 746-750.

Chang, C., Lue, A., and Zhang, L. 2008. Effects of crosslinking methods on structure and properties of cellulose/PVA hydrogels, Macromolecular Chemistry and Physics. 209. pp. 1266–1273.

Chavalparit, O., Rulkens, W.H., Mol, A.P.J., and Khaodhair, S. 2006. Options for environmental sustainability of the crude palm oil industry in Thailand through enhancement of industrial ecosystems. Environment, Development and Sustainability. 8(2). pp. 271-287.

Chotinantasaeth, S. 2007. Separation of lignin from black liquor by electrochemical process. Thesis of Master of Science. Chulalongkorn University.

Ciolacu, D., Kovac, J., Kokol, V. 2012. The effect of the cellulose binding domain from Clostridium cellulovorans on the supramolecular structure of cellulose fibers. Carbohydrate Research. 345. pp. 621–630.

De Rosa, E., Urciuolo, F., Borselli, C., Gerbasio, D., Imparato, G., and Netti, P.A. 2006. Time and space evolution of transport properties in agarose–chondrocyte constructs. Tissue Eng. 12. pp. 2193–2201.

Denizli, B.K., Can, H.K., Rzaev, Z.M.O., and Guner, A. 2004. Preparation conditions and swelling equilibria of dextran hydrogels prepared by some crosslinked agents, Polymer. 45(19). pp. 6431-6435.

Desbrieres, J., Hamcerencu, M., and Popa, M., and Riess, G. 2009. Stimuli-Sensitive Xanthan Derivatives/N-Isopropylacrylamide Hydrogels: Influence of Cross-Linking Agent on Interpenetrating Polymer Network Properties. Biomacromolecules. 10(7). pp. 1911-1922.

Domenek, S., Louaifi, A., Guinault, A., and Baumberger, S. 2013. Potential of lignins as antioxidant additive in active biodegradable packaging materials. Journal of Polymers and the Environment. 21(3). pp. 692–701.

Dong, J., Albertini, D.F., Nishimori, K., Kumar, T.R., Lu, N., and Matzuk, M.N. 1996. Growth differentiation factor-9 is required during early ovarian folliculogenesis. International of science. 383. pp. 531-535.

Duri, R.A., Lynch, B.M., and Sternhell, S. 1960. Comparative studies of brown coal and lignin. I. Infra-red spectra, Australian Journal of Chemistry. 13. pp. 156-165.

El-Mansouri, N.D. and Salvadó, J. 2007. Analytical methods for determining functional groups in various technical lignins. Industrial Crops and Products. 26. pp. 116-124.

Enkvist, T., and Alfredsson, B. 1953. Low Molecular Substances of Lignin Origin in Black Liquors from Sulphate and Soda Pulping of Spruce Wood. The Technical Association of Pulp and Paper Industry. 23. pp.24-32.

Epelde, I.G., Lindgren, C.T., and Lindström, M.E. 1998. Kinetics of Wheat Straw Delignification in Soda and Kraft Pulping. Journal of Wood Chemistry and Technology. 18. pp. 69-82.

Estellé, P., Halelfadl, S., and Maré, T. 2013. Lignin as dispersant for water-based carbon nanotubes nanofluids: Impact on viscosity and thermal conductivity. International Communications in Heat and Mass Transfer. 57. pp. 8-12.

Fache, M., Auvergne, R., Boutevin, B., and Caillol, S. 2015. New vanillin-derived diepoxy monomers for the synthesis of biobased thermosets. European Polymer Journal. 67. pp. 527-538.

Faria, S., Petkowicz, C.L.O., Morais, S.A.L., Terrones, M.G.H., Resende, M.M., França, F.P., and Cardozo, V.L. 2011. Characterization of xanthan gum produced from sugar cane broth. Carbohydrate Polymers. 86(2). pp. 469-476.

Fernández-Ronco, M.P., De Lucas, A., Rodríguez, J.F., García, M.T., and Gracia, I. 2013. New considerations in the economic evaluation of supercritical processes: separation of bioactive compounds from multicomponent mixtures, The Journal of Supercritical Fluids. 79. pp. 345–355.

Fukushima, R.S., Kerley, M.S., Ramos, M.S., Porter, J.H., and Kallenbach, R.L. 2015. Comparison of acetyl bromide lignin with acid detergent lignin and Klason lignin and correlation with in vitro forage degradability, Animal Feed Science and Technology. 201. pp. 25-37.

Garcia, A., Toledano, A., Serrano, L., Egues, I., Gonzalez, M., Marin, F., and Labidi, J. 2009. Characterization of lignins obtained by selective precipitation, Separation and Purification Technology. 68. pp. 193-198.

Garcia, A., Toledano, A., Serrano, L., Egues, I., Gonzalez, M., Marin, F., and Labidi, J. 2009. Characterization of lignins obtained by selective precipitation, Separation and Purification Technology. 68. pp. 193-198.

García, R., Lozano, G., Gabarrell, J., Rieradevall, G., Feijoo, and Murphy, R.J. 2008. Eco-innovation of a wooden childhood furniture set: An example of environmental solutions in the wood sector. Science of the Total Environment. 426. pp. 318-326.

García-González, C.A., Alnaief, M., and Smirnova, I. 2009. Polysaccharide-based aerogels promising biodegradable carriers for drug delivery systems. Carbohydrate Polymers. 86. pp. 1425–1438.

Gellerstedt, G. and Li, J. 2001. Non-desirable carbohydrate reactions in pulping and bleaching. Recent Advances in Environmentally Compatible Polymers. pp. 347-356.

Giles, P.S., Ray, D., and Sahoo, P.K. 2009. Characteristics of xanthan gum-based biodegradable superporous hydrogel. International Journal of Biological Macromolecules. 45. pp. 364-371.

Gilarranz, M.A., Oliet, M., Rodriguez, F., and Tijero, J. 1999. Methanol-based pulping of *eucalyptus globulus*. The Canadian Journal of Chemical Engineering. 77(3). pp. 515-521.

Grishechko, L.I., Labat, A., Fierro, V., Kuznetsov, B.N., Pizzi, A., and Celzard, A. 2013a. Tannin-based xerogels with distinctive porous structures. Industrial Crops and Products. 43. pp. 347–355.

Grishechko, L.I., Labat, A., Fierro, V., Kuznetsov, B.N., Szczurek, A., and Celzard, A. 2013b. Lignin–phenol–formaldehyde aerogels and cryogels. Microporous and Mesoporous Materials. 168. pp. 19-29.

Haghgoo, M., Yousefi, A.A., Zohouriaan Mehr, M.J., Celzard, A., Fierro, V., and Léonard, A. 2014. Characterization of multi-walled carbon nanotube dispersion in resorcinol-formaldehyde aerogels, Microporous and Mesoporous Materials. 184. pp. 97–104.

Haslach, H.W. 2000. The moisture and rate-dependent mechanical properties of paper: a review. Mechanics of Time Dependent Materials. 4. pp. 169-210.

Hergert, H.L., and Kurth, E.F. 1967. The infrared spectra of lignin and related compounds. I. Characteristic carbonyl and hydroxyl frequencies of some flavanones, flavones, chalcones and acetophenones, Journal of the American Chemical Society. 75. pp. 1622-1625.

Hirn, U., and Schennach, R. 2015. Comprehensive analysis of individual pulp fiber bonds quantifies the mechanisms of fiber bonding in paper. Naturalscience Journal. DOi: 10.1038/srep10503

Hofrichter, M. and Steinbuchel, A. 2001. Biopolymer : Lignin, Humic Substances and Coal. Vol. 1. New York: Weinheim: Wiley-VCH, pp. 89-127.

Ibarra, D., Rio, J.C., Gutiârrez, A., Rodriguez, I.M., Romero, J., MartÌnez, M.J., and MartÌnez, A.T. 2005. Chemical characterization of residual lignins from eucalypt paper pulps, Journal of Analytical and Applied Pyrolysis. 74. pp. 116-122.

Jeffries, M. 1994. Invertebrate communities and turnover in wetland ponds affected by drought. Freshwater Biology. 32(3). pp. 603-612.

Jiangyang, F., Wang, K., Liu, M., and He, Z. 2008. In vitro evaluations of konjac glucomannan and xanthan gum mixture as the sustained release material of matrix tablet. Carbohydrate Polymers. 73. pp. 241-247.

Karjalainen, M., Ammala, A., and Rousu, P. 2013. Fractionation of wheat straw pulp cells in a hydrocyclone. Nordic Pulp and Paper Research Journal. 28. pp. 282–289.

Kim, A., Margulies, M., and Egholm, M. 2005. Genome sequencing in microfabricated high-density picolitre reactors. Nature. 437. pp. 376-380.

Klapiszewski, Ł., Nowacka, M., Milczarek, G., and Jesionowski, T. 2013. Physicochemical and electrokinetic properties of silica/lignin biocomposites. Carbohydrate Polymers. 94(1). pp. 345-355.

Knoblauch, H., Heath, C., and Luff, P. 2000. Intermediate silicon layers detector for the CDF experiment. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment. 453. pp. 84-88.

Kubo, S., and Kadla, J.F. 2005. Lignin-based Carbon Fibers: Effect of Synthetic Polymer Blending on Fiber Properties, Journal of Polymers and the Environment. 13(2). pp. 97-105.

Lachenal, D., Mortha, G., Sevillano, R.M. and Zaroubine, M. 2004. "Isolation of Residual Lignin from Softwood Kraft Pulp. Advantages of The Acetic Acid Acidolysis Method" C.R. Biologies. 327. pp. 911-916.

Laura G.M., Méndez, J.A., Fernández-Gutiérrez, M., Vázquez, B., and San Román, J. 2014. Oxidized dextrins as alternative crosslinking agents for polysaccharides: Application to hydrogels of agarose–chitosan. Acta Biomaterialia. 10. pp. 798-811.

Le, Normand M., Edlund, U., and Holmbom, B. 2012. Hot-water extraction and characterization of spruce bark non-cellulosic polysaccharides. Nordic Pulp and Paper Research Journal. 27. pp. 18–23.

Lindenbaum, E.S., Tendler, M., and Beach, D. 1995. Serum-free cell culture medium induces acceleration of wound healing in guinea-pigs. Burns. 21. pp. 110-115.

Mano, J., Silva, G., Azevedo, H. S., Malafaya, P., Sousa, R., Silva, S., Boesel, L., Oliveira,J. M., Santos, T., and Marques, A. 2007. Natural origin biodegradable systems intissue engineering and regenerative medicine: Present status and some movingtrends. Journal of The Royal Society Interface. 4(17). pp. 999–1030.

Martin, B. C., Minner, E. J., Wiseman, S. L., Klank, R. L., and Gilbert, R. J. 2008. Hydrogelblends for support of nerve regeneration therapies. Journal of Neural Engineering. 5. pp. 221–231.

Methacanon, P., Weerawatsophon, U., Sumransin, N., Prahsarn, C., and Bergado, D.T. 2010. Properties and potential application of the selected natural fibers as limited life geotextiles, Carbohydrate Polymers. 82. pp. 1090-1096.

Millán, A.J., Nieto M.I., Moreno, R., and Baudín, C. 2002. Thermogelling polysaccharides for aqueous gelcasting – Part I: a comparative study of gelling additives. Journal of the European Ceramic Society. 22. pp. 2209–2215.

Min Zhang, Wu, C.X., Huang, J.Y., Peng, X.H., Chen, P., and Tang, S.Q. 2012. Synthesis and characterization of a degradable composite agarose/HA hydrogel. Carbohydrate Polymers. 88. pp. 1445-1452.

Ming, J., Xiao, C., Sun, J., Kang, S., and Bonasoni, P. 2010. Carbonaceous particles in the atmosphere and precipitation of the Nam Co region, central Tibet. Journal of Environmental Science. 22. Pp. 1748–1756.

Morris, E. R. 2009. Functional interactions in gelling biopolymer mixtures. In S. Kasapis, I. T. Norton, & J. B. Ubbink (Eds.), Modern biopolymer science. Amsterdam: Academic Press. pp.167-198.

Mukai, T., and Kuriyama, S. 2005. Geostatistical motion interpolation. ACM Transactions on Graphics. 24(3). pp. 1062-1070.

Mutalik, V., Manjeshwar, L.S., Wali, A., Sairam, M., Sreedhar, B., Raju, K.V.S.N., and Aminabhavi, T.M. 2007. Aqueous-solution and solid-film properties of poly(vinyl alcohol), poly(vinyl pyrrolidone), gelatin, starch, and carboxymethylcellulose polymers, Journal of Applied Polymer Science. 106. pp. 765–774.

Müller, K. 1986. Reports and reviews : Low-and-non-waste technology. Waste Management & Research. 4(1). pp. 226-228.

Mussatto, S.I., Dragone, G., and Roberto, I.C. 2007. Ferulic and p-coumaric acids extraction by alkalinehydrolysis of brewer’s spent grain. Industrial Crops and Products. 25. pp. 231-237.

Nada, A.M.A., El-Sakhawy, M. and Kamel, S.M. 1998. “Infrared Spectroscopic Study of Lignins” Polymer Degration and Stability. 60. pp. 247-251.

Narapakdeesakul, D., Sridech, W., and Wittaya, T. 2013a. Novel use of oil palm empty fruit bunch’s lignin derivatives for production of linerboard coating. Progress in Organic Coatings. 76. pp. 999– 1005.

Narapakdeesakul, D., Sridech, W., and Wittaya, T. 2013b. Synthesizing of oil palm empty fruit bunch lignin derivatives and potential use for production of linerboard coating. Songklanakarin J. Sci. Technol. 35(6). pp. 705– 713.

Navarra, J., Chang, C., Lu, A., and Zhang, L. 2005. Effects of Crosslinking Methods on Structure and Properties of Cellulose/PVA Hydrogels. Macromolecular Chemistry and Physics. 209(12). pp. 1266-1273.

Nenkova, S., 2007. Study of sorption properties of lignin – Derivatized fibrous composites for the remediation of oil polluted receiving waters. Bioresources. 2(3). pp. 408–418.

Nordstrand, T. 2003. Basic testing and strength design of corrugated board and containers. Ph.D. Thesis, Lund University, Sweden.

Norgren, M., Edlund, H., Wågberg, L., Lindström, B., and Annergren, G. 2001. Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: phase behavior. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 194. pp. 85-96.

Othmer, D.F. 1968. CORRELATING VAPOR PRESSURES AND VAPOR VOLUMES - Use of Reference Substance Equations. Industrial & Engineering Chemistry Research. 60(1). pp. 22-35.

Othmer, D.F. 1981. Encyclopedia of Chemical Technology. 2th ed. Vol 2. New York: John Wiley & Son. pp. 361-381.

Perissotto, D.O., Colodette, J.L., Nascimento, E.A. and Ramos, L.P. 2000. “Characterization of The Extractives Derived from Eucalyptus Kraft Pulping” Iberoamerican Congress Pulp and Paper Research.

Phitthayaphinant, P. and Nissapa, A. 2010. An Analytic Hierarchy Process (AHP) approach for the identification of unique and indigenous vegetables of southern provinces in Thailand – A key to promote tropical bio-diversity. Proceedings of the 7th IMT-GT UNINET and the 3rd International PSU- UNS Conferences on Bioscience, Songkhla, Thailand. 7-8 October 2010. pp. 62-67.

Pichainarong, W. 2002. Separation of lignin from eucalyptus pulping black liquor. Master’s thesis, Department of Graduate School, Chulalongkorn University.

Popescu, D.C., Ham, A.J.L., and Shieh, B.H. 2006. Scaffolding protein INAD regulates deactivation of vision by promoting phosphorylation of transient receptor potential by eye protein kinase C in Drosophila, Journal of Neuroscience. 26(33). pp. 8570-8577.

Raschip, I.E., Hitruc, E.G., Vasile, C., and Popescu, M.C. 2007. Effect of the lignin type on the morphology and thermal properties of the xanthan/lignin hydrogels. International Journal of Biological Macromolecules. 54. pp. 230-237.

Raschip, I.E., Hitruc, E.G., Oprea, A.M., Popescu, M.C., and Vasile, C. 2011. In vitro evaluation of the mixed xanthan/lignin hydrogels as vanillin carriers. Journal of Molecular Structure. 1003. pp. 67-74.

Raschip, I.E., Hitruc, E.G., Vasile, C., and Popescu, M.C. 2013. Effect of the lignin type on the morphology and thermal properties of the xanthan/lignin hydrogels. International Journal of Biological Macromolecules. 54. pp. 230-237.

Razzaghi, H., Oster, M., and Reefhuis, J. 2015. Long-Term Outcomes in Children with Congenital Heart Disease: National Health Interview Survey. The Journal of Pediatrics. 166(1). pp. 119-124.

Rincón, F., Muñoz, J., Ramírez, P., Galán, H., and Alfaro, M.C. 2011. Physicochemical and rheological characterization of Prosopis juliflora seed gum aqueous dispersions. Food Hydrocolloids. 35. pp. 348-357.

Rohella, R.S., Sahoo, N., Paul, S.C., Choudhury, S., and Chakravortty, V. 1996. Thermal studies on isolated and purified lignin. Thermochimica Acta. 287. pp. 131-138.

Román, I.L., White Jr., T.H., Barros, Y.M., and Develey, P.F. 2015. Improving reintroduction planning and implementation through quantitative SWOT analysis. Journal for Nature Conservation. 28. pp. 149-159.

Rosli, W.D., Chuah, S.B., and Ibrahim, M.N. 2004. Characterization of lignin precipitated from the soda black liquor of oil palm empty fruit bunch fibers by various mineral acids. ASEAN Journal on Science and Technology for Development. 21(1). pp. 57-67.

Rosli, R.E., Sulong, S.B., Daud, W.R.W., Haque, M.A., Zulkifley, M.A. 2017. A review of high-temperature proton exchange membrane fuel cell (HT-PEMFC) system. International Journal of Hydrogen Energy. 42(14). pp. 9293-9314.

Rushdan, I., Latifah, J., Hoi, W.K., and Mohd Nor, M.Y. 2007. Commercial-scale production of soda pulp and medium paper from oil palm empty fruit bunches. Journal of Tropical Forest Science. 19(3). pp. 121–126.

Sarkanen, K.V., Chang, H.M., and Ericsson, B. 1953. Species variation in lignins I infrared spectra of guaiacyl and syringyl models, Tappi. 50(11). pp. 572-575.

Saake, B,. and Lehnen, R. 2007. Size-exclusion chromatography of technical lignins in dimethyl sulfoxide/water and dimethylacetamide. Journal of Chromatography A. 1102. pp. 154-163.

Sehaqui, H., Salajková, M., Zhou, Q., and Berglund, L. 2010. Mechanical performance tailoring of tough ultra-high porosity foams prepared from cellulose I nanofiber. Soft Matter. 8. pp. 1824-1832.

Shen, F., Fu, Y., Wang, G., Mei, T., and Wang, X. 2016. Accessible Graphene Aerogel for Efficient Harvesting Solar Energy. ACS Sustainable Chemistry & Engineering. 5(6). pp. 4665-4671.

Sjostrom, E. 1981. Wood Chemistry Fundamentals and Applications. Findland: Harcourt Brace Jovanovich. pp. 68-82, 104-144.

Sjostrom, E. and Alen, R. 1999. Analytical Methods in Wood Chemistry, Pulping, and Papermaking. New York: Springer-Verlag Berlin Heidelberg. pp. 221-222.

Socrates, G. 2004. Organic Halogen Compounds, in: Infrared and Raman Characteristic Group Frequencies: Tables and Charts 3rd edition. JohnWiley & Sons Ltd. Chichester. pp. 198–208.

Sridach, W. 2010. The Environmentally benign pulping process of non-wood fibers. Suranaree Journal of Science and Technology. 17(2). pp. 105.123.

Sun, R.C., Tomkinson, J., and Bolton, J. 1999. Effects of precipitation pH on the physicchemical properties of the lignins isolated from the black liquor of oil palm empty fruit bunch fiber pulping, Polymer Degradation and Stability. 63. pp. 195-200.

Sun, R.C., Tomkinson, J., and Bolton, J. 2001. Separation and Characterization of Lignins from The Black Liquor of Oil Palm Trunk Fiber Pulping. Separation Science and Technology. 34(15). pp. 3045-3058.

Sun, R.C., Tomkinson, J., and Jones, G.L. 2010. Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. Polymer Degradation and Stability. 68. pp. 111-119.

Szczurek, A., Jurewicz, K., Amaral-Labat, A., Fierro, V., Pizzi, A., and Celzard, A. 2010. Structure and electrochemical capacitance of carbon cryogels derived from phenol–formaldehyde resins. Carbon. 48(13). pp. 3874-3883.

Szczurek, A., Amaral-Labat, A., Fierro, V., Pizzi, A., Masson, E., and Celzard, A. 2011. The use of tannin to prepare carbon gels. Part I: Carbon aerogels. Carbon. 49(8). pp, 2773-2784.

Tanistra, I. and Bodzek, M. 1998. “Preparation of High-Purity Sulphate Lignin from Spent Black Liquor Using Ultrafiltration an Dialfiltration Processes” Desalination. 115. pp. 111-120.

TAPPI: T222-om-02. Technical Association of the Pulp and Paper Industry 1983 (reaffirmation in 2006).

TAPPI: T818. Technical Association of the Pulp and Paper Industry 1983 (reaffirmation in 2006).

Tejado, A., Pena, C., Labidi, J., Echeverria, J.M., and Mondragon, I. 2007. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis, Bioresource Technology. 98. pp. 1655-1663.

Thakur, V.K., Thakur, M.K., Raghavan, P., and Kessler, M.R. 2014. Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. ACS Sustainable Chemistry & Engineering. 2(5). pp. 1072-1092.

Theliander H. 2007. Recovery of cooking chemicals; the treatment and burning of black liquor. In Ljungberg textbook. Pulp and Paper Chemistry and Technology. Book 2. Pulping Chemistry and Technology Ed(s). Ek M, Gellerstedt G and Henriksson G, Fiber and Polymer Technology, KTH, Stockholm.

Trivedi, T.J., Rao, K.S., and Kumar, A. 2014. Facile preparation of agarose–chitosanhybrid materials and nanocomposite ionogels using an ionic liquid viadissolution, regeneration and sol–gel transition, Green Chemistry. 16(1). pp. 320–330.

Varoni, E., Tschon, M., Palazzo, B., Nitti, P., Martini, L., and Rimondini, L. 2012. Agarosegel as biomaterial or scaffold for implantation surgery: Characterization, histo-logical and histomorphometric study on soft tissue response. Connective TissueResearch. 53(6). pp. 548–554.

Vasileva, T.E., and Gushterova, M.N. 2007. New Protein Hydrolysates from Collagen Wastes Used as Peptone for Bacterial Growth. Current Microbiology. 54(1). pp. 54-57.

Veronovski, A., Tkalec, G., Knez, Z., and Novak, Z. 2014. Characterisation of biodegradable pectin aerogels and their potential use as drug carriers. Carbohydrate Polymers. 113. pp. 272-278.

Vilgis, T.A. 2005. Time scales in the reinforcement of elastomers. Polymer. 46(12). pp. 4223-4229.

Vinardell, M.P., Ugartondo, V., and Mitjans, M. 2008. Potential applications of antioxidant lignins from different sources. Industrial Crops and Products. 27(2). pp. 220-223.

Vishtal, A.G., and Kraslawski, A. 2011. Challenges in Industrial Applications of Technical Lignins. BioResource. 6(3). pp. 56-63.

Wallberg, O., Jönsson, A.S., and Wimmerstedt, R. 2003. Ultrafiltration of kraft black liquor with a ceramic membrane. Desalination. 156. pp. 145–153.

Wörmeyer, K., and Smirnova, I. 2014. Breakthrough measurements of CO_2 through aminofunctionalised aerogel adsorbent at low partial pressure: Experiment and modeling. Microporous and Mesoporous Materials. 184. pp. 61-69.

Yamada, Y., Hozumi, K., Aso, A., Hotta, A., Toma, K., and Katagiri, F. 2012. Laminin active peptide/agarose matrices as multifunctional biomaterials for tissue engineering. Biomaterials. 33. pp. 4118–4125.

Yamaguchi, A., Isozaki, K., Nakamura, M., Takaya, H., and Watanabe, T. 2016. Discovery of 12-mer peptides that bind to wood lignin. Scientific Reports. 6(1). https://doi.org/10.1038/srep21833

Yawalata, D. and Paszner, L. 2004. Anionic effect in high concentration alcohol organosolv pulping. Holzforschung., 58(1). pp. 1–6.

Yuan, T.Q., He, J., Xu, F., and Sun, R.C. 2009. Fractionation and physico-chemical analysis of degraded lignins from the black liquor of Eucalyptus pellita KP-AQ pulping. Polymer Degradation and Stability. 94. pp. 1142-1150.

Zhang, J., Choi, Y.S., and Yoo, Ch.G. 2014. Cellulose–Hemicellulose and Cellulose–Lignin Interactions during Fast Pyrolysis. Chemical and Biological Engineering. 3(2). pp. 293-301.

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List of Publication and Proceedings

S. Sathawong, W. Sridach, and K.A. Techato. Characteristics of lignin-agarose hydrogel from oil palm empty fruit bunches' black liquor. 3rd International congress on technology - engineering & science. Asia Pacific University of Technology & Innovation (APU) on Feb 9-10, 2017, Malaysia.

S. Sathawong, W. Sridach, and K.A. Techato. Recovery of Kraft Lignin from OPEFB and Using for Lignin-Agarose Hydrogel. Journal of Polymers and The Environment. https://doi.org/10.1007/s10924-018-1218-3.

S. Sathawong, W. Sridach, and K.A. Techato. Lignin: Isolation and preparing the lignin based hydrogel. Journal of Environmental Chemical Engineering. https://doi.org/10.1016/j.jece.2018.05.008