UNIVERSITI PUTRA MALAYSIA

EFFECT OF MACERATION TIME ON CHARACTERISTICS OF ACID-HYDROLYZED CELLULOSE FROM PINEAPPLE LEAF

NAZIRATULASIKIN BINTI ABU KASSIM

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By

NAZIRATULASIKIN BINTI ABU KASSIM

**Thesis submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the Requirements for the Master of Science**

March 2018

This thesis is dedicated to:

My beloved parents;

Abu Kassim Mohd Sani & Che Puan Abd Hamid

My siblings;

My dearest friends;

Thank you

Abstract of a thesis presented to the Senate of Universiti Putra Malaysia
in fulfilment of the requirement for the degree of Master of Science

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March 2018

Chairman : Associate Professor Edi Syams Zainudin, PhD
Institute : Tropical Forestry and Forest Products

Recently, the utilisation of other non-wood materials as well as crop residues have attracted global attention due to their environmentally friendly and feasible properties once becomes a product. Pineapple leaf is a residue of fresh fruit for domestic used and canned pineapple industry. This residue was produced in large scale quantities and relatively inexpensive source. Pineapple leaf can be utilised as a potential source of isolating cellulose in micro and nano scale dimensions of cellulose. In order to attain such celluloses, some pre-treatment and acid hydrolysis process was performed in controlled conditions. The chlorinated solvents were widely consumed in certain industries to produce high purity of cellulose, though chlorine is toxic and harmful to environment. Maceration approach was introduced to overcome the increasing of environment concern. Hence, the aim of this study was to isolate cellulose by introducing maceration method via hydrogen peroxide and acetic acid at 80°C. This treatment also plays with variables of maceration duration (TF-2, TF-3, and TF-4) to get the best results of obtained cellulose. The process for the acid-hydrolyzed part comprising the macerated cellulose to further on acid hydrolysis process by considered some factors such as acid concentration, temperature, hydrolysis time, and pulp-to-acid ratio. The macerated cellulose was treated with 64 %w/w of sulfuric acid, 45 °C temperature, 45 min and 60 min (for TF-4) of hydrolysis time, 1:30 of pulp-to-acid ratio, and 20 minutes of sonication time. Resultant cellulose was tested for chemical composition, morphological observation, thermogravimetric analysis, Fourier Transform Infrared spectroscopy analysis, and crystallinity index. It was shown that the best maceration treatment was TF-3 (3 hours maceration time) and followed by TF-2 and TF-4 by considering its cellulose composition. By conducting maceration treatment, results revealed that pineapple leaf for TF-3 has cellulose content which is 70.92%. Results also demonstrated that mainly hemicellulose and residual lignin remains after the maceration treatment. It was expected because maceration treatment was used. Maceration treatment also has been found successfully decreased macerated cellulose diameter and length. Prior to acid hydrolysis treatment, the decreasing of acid-hydrolyzed diameter was attained. The lowest diameter for acid-hydrolyzed cellulose was 111.6 nm. By performing acid hydrolysis treatment, the crystallinity

index for acid-hydrolyzed cellulose was increased. Highest crystallinity index for acid-hydrolyzed cellulose was 69.30% for AC-345 compared to original raw material which is 43.70%. Higher thermal degradation was found in macerated cellulose and acid-hydrolyzed cellulose was 338°C and 337°C, respectively. In conclusion, pineapple leaf was found as potential source of purified cellulose with some modifications needed prior to produce a product or as reinforcement in other materials such as composites field.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KESAN TEMPOH MASERASI TERHADAP CIRI-CIRI SELULOSA-TERHIDROLISIS DARIPADA DAUN NANAS

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NAZIRATULASIKIN BINTI ABU KASSIM

Mac 2018

Pengerusi : Profesor Madya Edi Syams Zainudin, PhD
Institut : Perhutanan Tropika dan Produk Hutan

Kebelakangan ini, penggunaan bahan bukan kayu begitu juga sisa tanaman telah menarik perhatian kerana mesra alam dan mempunyai sifat-sifat yang praktikal apabila menjadi sesuatu produk. Daun nanas adalah tinggalan daripada penggunan buah segar untuk kegunaan domestik dan industri pengenitanan buah nanas. Hasil tinggalan ini dihasilkan dalam kuantiti skala yang besar dan ianya merupakan sumber yang jimat kos. Daun nanas juga boleh digunakan sebagai sumber yang berpotensi dalam menghasilkan selulosa dalam mikro dan juga skala dimensi nano. Bagi menghasilkan selulosa ini, sedikit pra rawatan dan proses hidrolisis asid dalam keadaan yang dikawal yang tertentu perlu dijalankan. Pelarut berklorin telah digunakan secara meluas dalam sesetengah industri dalam penghasilan selulosa berfurifikasi tinggi, walaupun klorin adalah bersifat toksik dan berbahaya kepada persekitaran. Kaedah maserasi seterusnya diperkenalkan bagi menangani peningkatan kebimbangan terhadap persekitaran ini. Justeru, matlamat kajian adalah untuk mengahasilkan selulosa dengan memperkenalkan kaedah maserasi melalui hidrogen peroksida dan asid asetik pada suhu 80°C. Rawatan ini juga dijalankan dengan pelbagai durasi maserasi untuk mendapatkan keputusan terbaik bagi selulosa yang akan dihasilkan. Proses bagi bahagian hidrolisis asid terdiri daripada selulosa maserasi yang dilanjutkan kepada proses hidrolisis asid dengan mengambil kira beberapa faktor seperti kepekatan asid, suhu, tempoh hidrolisis, dan nisbah pulpa kepada asid. Selulosa maserasi ini telah dirawat dengan asid sulfurik 64 %w/w, suhu 45 °C, masa hidrolisis asid selama 45 dan 60 minit (untuk TF-4), nisbah 1:30 pulpa kepada asid, dan 20 minit masa untuk sonifikasi. Selulosa yang terhasil telah diuji untuk komposisi kimia, pemerhatian morfologi, analisis termal, analisis *Fourier Transform Infrared spectroscopy*, dan indeks kristaliniti. Keputusan kajian menunjukkan selulosa terbaik bagi rawatan maserasi adalah pada TF-3 (3 jam tempoh maserasi) dan diikuti dengan TF-2 dan TF-4 dengan mengambil kira komposisi kimianya. Dengan melakukan rawatan maserasi, keputusan mendapati daun nanas bagi TF-3 mempunyai kandungan selulosa sebanyak 70.92%. Keputusan kajian juga mendapati kebanyakan hemiselulosa dan baki lignin masih didapati selepas rawatan maserasi. Ini adalah dijangkakan memandangkan rawatan maserasi digunakan. Rawatan maserasi juga telah didapati berjaya mengurangkan diameter dan panjang

selulosa maserasi. Seiring itu juga, dengan rawatan hidrolisis asid penurunan diameter selulosa terhidrolisis asid juga berjaya dicapai. Diameter terendah bagi selulosa terhidrolisis asid ialah 111.6 nm. Dengan menjalankan rawatan hidrolisis asid, indeks kristaliniti bagi selulosa terhidrolisis asid didapati meningkat. Indeks kristaliniti bagi selulosa terhidrolisis asid tertinggi adalah 69.30% bagi AC-345 berbanding dengan bahan mentah yang asal iaitu sebanyak 43.70%. Pemerosotan termal tertinggi didapati dalam selulosa maserasi dan selulosa terhidrolis asid adalah masing-masing pada 338°C dan 337°C. Sebagai kesimpulan, daun nanas didapati sesuai untuk digunakan sebagai sumber yang berpotensi sebagai selulosa berfurifikasi dengan sedikit modifikasi perlu dilakukan terhadap selulosa ini dalam menghasilkan sesuatu produk atau sebagai bahan pengukuhan dalam material lain seperti dalam bidang komposit.

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I certify that a Thesis Examination Committee has met on (date of viva) to conduct the final examination of Naziratulasikin binti Abu Kassim on her master of science thesis entitled "Effect of Maceration Time on Characteristics of Acid-Hydrolyzed Cellulose from Pineapple Leaf" in accordance with the Universities and Universities Collegue Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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Associate Professor
Faculty of Biotechnology and Biomolecule Sciences
Universiti Putra Malaysia
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Umi Kalsom Md Shah, PhD
Associate Professor
Faculty of Biotechnology and Biomolecule Sciences
Universiti Putra Malaysia
(Internal Examiner)

Wan Aizan Wan Abdul Rahman, PhD
Associate Professor
Faculty of Engineering
Universiti Teknologi Malaysia
(External Examiner)

RUSLI HAJI ABDULLAH, PhD
Professor and Deputy Dean
Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Edi Syams Zainudin, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Ainun Zuriyati Mohamed @Asa'ari, PhD
Research Officer
Institute of Tropical forestry and Forest Product
Universiti Putra Malaysia
(Member)

Sarani Zakaria, PhD
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Member)

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Name of Chairman of Supervisory Committee : Assoc. Prof. Dr. Edi Syams Zainudin

Signature : ______________________________

Name of Member of Supervisory Committee : Dr. Ainun Zuriyati Mohamed@ Asa'ari

Signature : ______________________________

Name of Member of Supervisory Committee : Prof. Dr. Sarani Zakaria

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LIST OF ABBREVIATIONS

PAA	Peracetic acid
FTIR	Fourier transform infrared
FESEM	Field emission scanning electron microscope
PALF	Pineapple leaf fiber
GPa	Giga Pascal
µm	micro meter
g/den	gram per density
MPa	mega Pascal
g/m^3	gram per meter cubic
AFM	Atomic force microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
MCC	Microcrystalline cellulose
DMA	Dynamic mechanical analyzer
H_2O_2	Hydrogen peroxide
CH_3COOH	Acetic acid
TAPPI	Technical Association of Pulp and Paper Industry
$NaClO_2$	Sodium chlorite
NaOH	Sodium hydroxide
CrI	Crystallinity index
w/w	weight per weight
kV	kilo volt
nm	nanometer

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Cellulose is the most abundant natural polymer that can be applied in numerous fields and also contributed in industrial all over the world. Due to environmental concern such as deforestation, global warming, pollution and other environmental issues, people nowadays have shifted their preferences of using wood to another alternative source to save the earth. Reuse of agro wastes will lead to a significant reduction of generated waste hence decreased environmental impact.

Natural fibers are not only immanent throughout the world, but the fibres which also referred as a cellulosic fiber is related to the main chemical component cellulose or as a lignocellulosic fiber, since the fibers usually contain natural polyphenolic polymer and lignin in their structure (Azizi, Alloin & Dufresne, 2005). They are can be categorized into a few subgroups according to their sources such as grasses, reeds, stalks, bast fibers, leaf fibers, non-wood fibers, and woody vegetation. Currently, cellulosic fiber from non-wood resources such as kenaf, *Mengkuang* leaves, bamboo, jute, hemp, banana rachis and many other cellulosic sources are widely used as an alternative to wood due to the depletion of wood supply. Moreover, fiber agricultural crop residues such as rice husk, wheat straw, banana stem, grape skin, potato peel, soy hulls and pineapple residues which were focused on their leaves have been studied and developed to utilize in many applications.

Pineapple is one of the most familiar tropical fruits widely cultivated around the world cardinally for its fruits in the commercialization of fresh fruit, canned products and its juice. According to the Ministry of Agriculturae and Agro-Based Malaysia, pineapple plays an important role in exportation sector after banana and further seeking high demand in global market. The productivity is expected to growth rapidly concerning the initiatives done by the certain organization and farmers in order to boost the productions. This is reported by Malaysian Pineapple Industry Board that an annual positive increase in the area of planted pineapple comprises over 8000 hectares in 2011. However, the pineapple’s major part which is leaf is currently unused and needs a global attention for its commercial exploitation. After fruit harvesting, the leaves derived in considerable quantities by farmers and food industries are disposed of by burning process or decomposed. This happened due to the outdated technology involved for this purpose and ignorance from farmers and local communities regarding the existence of commercial uses of pineapple leaves. It is reported that from the year 2008 until 2010, there are about 85-88% of pineapple leaves have been wasted (Yusof, Yahya, & Adam, 2015).

This issue is addressed by a few studies reported that the leaf has been utilized as a raw material for industrial applications due to its auspicious values in terms of processing and producing. Previous research findings regarding pineapple leaf have been implemented and showed a promising result at different fields of application. Pineapple leaf cellulose offers a tremendous potential as a native fibrous constituent in mechanical performance defeating the other plant fibers in current commercial products. This advantage would enhance the competitiveness of pineapple residues as an alternative raw material in manufacture industry.

Pineapple leaf cellulose has been used in many fields such as in composite manufacture, textiles, pharmaceutical, pulp and paper making and many more. As a result of its versatility, there are a lot of methods have been reported to extract the cellulose from its raw material. The chemical, mechanical, thermal as well as combination treatment for extraction of delignified cellulose has been studied previously.

The maceration treatment was designed to completely digest the non-cellulosic compositions. Maceration process referred to any materials that soaked and heated with chemicals such as hydrogen peroxide and acid acetic until separated into a different constituent element. In addition, hydrogen peroxide is frequently applied as a good bleaching agent. Even though, maceration process is a quite similar with peracetic acid treatment (PAA) because of the usage of acetic acid and hydrogen peroxide, maceration according to Reddy & Yang (2007), is usually practised in one of the procedures in measuring biometrics of certain raw materials in terms of fiber length, fiber width and more in the individual cellulose form. This process may change the physics of raw material from chip to fibrous form, from unbleached to the bleaching stage which is due to the removal of some amount of lignin.

It is known that pineapple leaf is one of the plants that have high contents of cellulose and these cellulose molecules are in ordered strand arrangement and organized into larger structure to make up the cell wall of the plants. Since nearly all of the cell wall cellulose is crystalline, this cellulose has great commercial value when formed into products. Thus, when this cell wall cellulose was treated with sulfuric acid hydrolysis, esterification of hydroxyl groups is involved to yield acid half-ester or also can be called as 'cellulose sulphate'. The attachment of sulphate groups on the surface of hydrolyzed cellulose results in negatively charged surfaces above acidic pH. This anionic stabilization via the repulsion forces of electrical double layers was exhibited to be very effective in preventing the aggregation of resultant cellulose (Satyamurthy & Vigeshwaran, 2013). In acid hydrolysis process, this treatment essentially removes noncellulose components and most amorphous csegments from the material and produce cellulose with high crystalline region. Cellulose in nanoscale dimensions isolated by means of acid hydrolysis may resulted in vary of its morphology and dimensions, depending on the controlled conditions applied during the process. It is important to take into account that only amorphous segments were attacked by the acid and keep the crystalline segments remain intact. The successful of acid hydrolysis treatment performed on the materials depending on several factors including hydrolysis time, temperature, and acid concentration used (Pirani & Hashaikeh, 2013).

1.2 Problem Statement

Numerous studies have been done on the production of various size of cellulose from pineapple leaf by conducting different kinds of pre-treatments such as steam explosion, alkali treatment, water retting, milling technique, Kraft pulping, and soda pulping. In this study, maceration process was used as a pre-treatment method. Maceration is set up by mixing up acid acetic with hydrogen peroxide and then heated for several duration of time to determine the effectiveness of the pre-treatment.

In order to achieve a minimum dimension of cellulose's size, acid hydrolysis method was selected as the practical approach used in order to isolate the nanoscale dimension of cellulose. The function of acid hydrolysis is to provide the negative surface charge to assist on hydrolysing the amorphous regions. In contrast, even various strong acids can be used; each of them provides a different function. It is noted that sometimes acid hydrolysis is not a promising way to get cellulose in least nanoscale dimensions although the amorphous regional parts are hydrolyzed because of several factors. The pursuance of cellulose depending on the originality of the cellulose source as well as acid hydrolysis reaction conditions (i.e., acid type and concentration, reaction time and temperature) and thus resulted in different physical and mechanical properties on cellulose structures yield.

Plant materials need to be in separated fiber materials form first which known as pulp, before made into paper product. During this state, chlorite is used to bleach the pulp to make it brighter which makes it desirable for consumers. In pulp and paper industry, the common technique to bleach the pulp involves number of steps, depending on the nature of the pulp. Commonly, chlorinated solvent such as sodium chlorite and sodium hypochlorite was widely consumed to remove the lignin. These chemicals commonly are low-cost and act as most effective bleaching agent. However, results by using these solvents were the emission of organo-chloride compounds which are harmful to the environment. To overcome this issue as it is expected to reduce the impact of pollution to the environment, alternative approach such as maceration technique was introduced in this study.

To avoid the utilisation of chlorinated solvent such as sodium chlorite and sodium hypochlorite, maceration approach was introduced as pre-treatment in order to isolate the cellulose as well as to delignify the cellulose. Maceration treatment was dissimilar with standard bleaching procedure conducted to bleach the fiber. The treatment using maceration technique was conducted at 80 °C with variation of time to remove the lignin and unlike the bleaching process which ordinarily involves few sequences; 3 hours per sequence and conducted at 70 °C.

1.3 Objective

The aim of this study was to comprehend the potential in terms of properties of macerated and acid-hydrolyzed cellulose from pineapple leaf.

The specific objective of this study was to evaluate the effect of maceration duration on the characteristics of macerated and acid-hydrolyzed cellulose.

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BIODATA OF STUDENT

Naziratulasikin binti Abu Kassim was born on Jauary 24, 1989 at Kuala Kangsar, Perak. She got her Bachelor of Science degree in Wood Fiber Technology and Industry from Universiti Malaysia Sabah in 2011. The author was the continued her study under Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia under supervision of Assoc. Prof. Dr. Edi Syams Zainudin and co-supervision of Dr. Ainun Zuriyati Mohamed @Asa'ari . She joined as a postgraduate student in Master of Science in Pulp and Paper Technology as her field of study.

LIST OF PUBLICATIONS

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Naziratulasikin Abu Kassim, Ainun Zuriyati Mohamed, edi Syams Zainudin, Sarani Zakaria, Siti Kahulah Zakiah Azman & Hazwani Husna Abdullah. 2019. Isolation and characterization of macerated cellulose from pineapple leaf. *Bioresources.com*, 14(1), 1198-1209.

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