OPTIMIZATION AND THERMAL DEGRADATION KINETICS OF CELLULOSE NANOPARTICLES (CNPs) PRODUCTION FROM COCONUT FIBER

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2021

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by

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Project report submitted in partial fulfilment of the requirement for the degree of

Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENT

This final year project is for the completion of degree of Bachelor of Engineering (Chemical Engineering) with Honours at Universiti Sains Malaysia. I would like to take this opportunity to show my highest gratitude and appreciation towards all the individuals and authorities who assist me throughout this project.

First and foremost, I would like to express deepest gratitude towards my final year project supervisor, Associate Professor Dr. Khairiah Abd. Karim from Chemical Engineering of Universiti Sains Malaysia (USM) for the guidance, supervision and encouragement throughout the research project. Without your support in both mentally and emotionally, the progression of the report would not be smooth and steady. Thank you also for supplying the data for optimization process and thermal degradation kinetics from the thesis to assist me in completing my final year project.

Besides, I would like to thank Universiti Sains Malaysia (USM) Engineering Campus for providing me the accommodation and facilities especially during this COVID-19 pandemic, so that I have no worry on my daily life issue, enables me to keep focus on completing my project.

Apart from that, I would like to express highest gratitude towards my family members, course mates and fellow friends for the endless support and encouragement. Thank you to my roommates for the willingness to share joy, sorrow, knowledges and ideas.

Once again, I thank to all the individuals and authorities who assisted and supported me directly or indirectly throughout the project completion, including those who I missed to mention on. Thank you very much.

Tim Mau Sean

June 2021

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Extraction time/ Pre-exponential coefficient	mins/ -
B	Extraction temperature	°C
b_0	Constant coefficient	-
b_1, b_2, b_3	Linear coefficients	-
b_{11}, b_{22}, b_{33}	Quadratic coefficients	-
b_{12}, b_{13}, b_{23}	Interaction coefficients	-
C	CF:IL ratio	w/w
$C.V.$	Coefficient of variation	%
E_a	Activation energy	kJ/mol
$f(\alpha)$	Differential reaction model	-
$g(\alpha)$	Integral reaction model	-
$k(T)$	Temperature dependent rate constant	
L	Length	nm
R	Gas constant	J/K/mol
R^2	Coefficient of determination	-
W	Width	nm
W_o	Initial mass of sample	-
W_t	Mass of sample at time, t	-
W_∞	Final mass of sample	-
t	Time	-
T	Absolute temperature	K
Y	Response/ Ultrafine CNPs distribution	- / %

α	Axial distance/ Conversion	- / %
β	Heating rate	°C/min

LIST OF ABBREVIATIONS

Symbol	Descriptions
2D	Two-dimensional
3D	Three-dimensional
ANOVA	Analysis of variance
BMIM (Cl)	1-butyl-3-methylimmidazolium chloride
CCD	Central-Composite-Design
CF	Coconut fibers
CNPs	Cellulose nanoparticles
CNFs	Cellulose nanofibers
CNCs	Cellulose nanocrystals
CNWs	Cellulose nanocrystals
DOE	Design of experiment
DTG	Derivative thermogravimetric
FWO	Flynn-Wall-Ozawa
IL	Ionic liquid
KAS	Kissinger-Akahira-Sunose
RSM	Response surface methodology
TGA	Thermogravimetric analyser

PENGOPTIMUMAN DAN KINETIK DEGRADASI TERMAL UNTUK NANOPARTIKEL SELULOSA (CNPS) PENGHASILAN DARIPADA SERAT KELAPA

ABSTRAK

Pengoptimuman dan kinetik degradasi termal untuk penghasilan nanopartikel selulosa (CNPs) daripada serat kelapa telah ditunjukkan dalam projek penyelidikan ini. Projek penyelidikan ini dijalankan dengan menggunakan data yang dikumpulkan daripada tesis yang bertajuk 'Dissolution of Natural Fiber using Ionic Liquid for Production of Cellulose Nanoparticles' oleh Nadzirah binti Yahya. Untuk bahagian pengoptimuman, penghasilan CNPs daripada serat kelapa telah disimulasikan menggunakan Kaedah Permukaan Sambutan (RSM) melalui Rekabentuk Komposit-Pertengahan (CCD) dalam perisian Design Expert untuk menentukan hubungan antara parameter yang mempengaruhi (masa pengekstrakan, suhu pengekstrakan dan nisbah serat kelapa (CF) kepada cecair ionic (IL)) pada tindak balas (pengagihan CNP yang sangat halus). Hasil simulasi menunjukkan bahawa kedua-dua suhu pengekstrakan dan nisbah CF: IL lebih signifikan terhadap model regresi. Pengagihan CNP ultrahalus maksimum yang diperolehi melalui proses pengoptimuman ialah 58.074%, dalam keadaan operasi selama 30 minit untuk masa pengekstrakan, 69.518 °C untuk suhu pengekstrakan dan 0.01 w/w untuk nisbah CF:IL. Untuk kajian kinetik degradasi termal CNPs yang dihasilkan daripada serat kelapa, kedua-dua kaedah isokonversional yang bebas model, Kissinger-Akahira-Sunose (KAS) dan Flynn-Wall-Ozawa (FWO) telah digunakan untuk menentukan tenaga pengaktifan, E_a untuk CNPs yang telah dihasilkan. Walau bagaimanapun, hasil E_a yang dikira tidak memuaskan, nilai E_a yang didapati adalah dalam julat -0.039 hingga -3.134 kJ/mol. Nilai E_a yang didapati sangat menyimpang daripada nilai E_a untuk CNPs yang

biasa. Sumber ralat ini diramalkan berasal daripada hasil yang tidak tepat daripada data yang telah dikumpulkan.

OPTIMIZATION AND THERMAL DEGRADATION KINETICS OF CELLULOSE NANOPARTICLES (CNPS) PRODUCTION FROM COCONUT FIBER

ABSTRACT

Optimization and thermal degradation kinetics of the cellulose nanoparticles (CNPs) production from coconut fibers were presented in this research project. The research project was carried out by using the data collected from the thesis with the title of 'Dissolution of Natural Fiber using Ionic Liquid for Production of Cellulose Nanoparticles' by Nadzirah binti Yahya. For optimization part, the CNPs production from coconut fibers was simulated using the Response Surface Methodology (RSM) via Central Composite Design (CCD) in Design Expert software to determine the relationship between the affecting parameters (extraction time, extraction temperature and ratio of coconut fiber (CF) to ionic liquid (IL)) on the response (ultrafine CNPs distribution). The simulation results showed that both the extraction temperature and CF:IL ratio were more significant to the regression model. The maximum ultrafine CNPs distribution obtained through the optimization process was 58.074 %, under the operating conditions of 30 mins of extraction time, 69.518 °C of extraction temperature and 0.01 w/w of CF:IL ratio. For the thermal degradation kinetics study of CNPs produced from coconut fibers, both the model-free isoconversional Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods were used to determine the activation energy, E_a of the CNPs. However, the calculated results of E_a were not satisfied, which were ranged from -0.039 to -3.134 kJ/mol. The values deviated very much from the E_a value of common CNPs, and the possible source of error was predicted to be from the inaccurate results from the collected data.

CHAPTER 1 INTRODUCTION

1.1 Background

Cellulose was established in 1838 by a French scientist, Anselme Payen (Wertz, Bédué and Mercier, 2010). He named the special structure in the fibrous component of all the higher plant cell as cellulose. Since the cellulose are arranged in micro-fibrils bundles, hence it provides high stability to plant structure and becoming the main molecule in the plant cell wall due to its superior strength and mechanical properties (Wertz, Bédué and Mercier, 2010; Brigham, 2018). Cellulose not only synthesized by plants, some of the bacteria, protozoans, fungi, algae and animal tunicates also producing it, hence cellulose is one of the most abundant biomaterials in the biosphere (Wertz, Bédué and Mercier, 2010).

With the advancement of technology and industrial revolutions, nanotechnology is becoming an important field and has the potential to create many possibilities. Nanotechnology is defined as the knowledge and understanding on the control of matter in at least one dimension measurement range from 1 to 100 nm (Börjesson and Westman, 2015). Despite cellulose has been known for around 150 years, cellulose nanoparticles have emerged and becoming an outstanding material in recent years and has attracted the attention of most the scientists and researchers due to its several advantages. In general, cellulose nanoparticles offer high tensile strength and stiffness, good electrical and thermal properties, higher surface area to volume ratio, higher hydrogen-bonding capacity, better sustainability, higher availability, non-toxicity, more eco-friendly, and better biocompatibility (Börjesson and Westman, 2015; Trache *et al.*, 2020).

There are many sources for cellulose fibers extraction to produce cellulose nanoparticles (CNPs). The feedstock has a broad range of animals, plants, and bacteria. The feedstock for CNPs production is very important, as it may affect the extraction methods and

the size and properties of the CNPs. The CNPs can be produced by mechanical, chemical, and enzymatic treatments, or a combination of these methods (Trache *et al.*, 2020)**.**

In this project, coconut fiber was chosen to be the feedstock to produce into cellulose nanoparticles (CNPs) since it is a lignocellulosic material which has high cellulose content. In order to optimize the production of cellulose nanoparticles (CNPs) from coconut fiber, response surface methodology (RSM) was applied. In 1951, RSM was developed by Box and Wilson in order to improve the manufacturing processes in chemical industry, for example by increasing the product yield and purity and reducing the production cost (Dean, A., Voss, D., & Draguljić, 2017)**.** Besides, the thermal degradation kinetics of the CNPs produced was studied in order to determine their thermal stability.

1.2 Problem Statement

The wastes accumulation in our world is kept on increasing due to the higher ability of purchasing from the consumers which lead to increasing in demands and production of consumer goods. Therefore, the use of green, renewable, and sustainable resources in the production of diverse high-value products with low environmental impact has grown increasingly essential in recent years. Hence, a number of solutions have been proposed by scientists and researchers and one of the most common method is by converting the wastes into useful consumer goods which not only can be sold and becoming a potential industry, at the same time reducing the waste accumulations. Cellulose, a fascinating polymer which is available abundantly and has great potential to be modified and functionalized to serve different industrial uses. In Malaysia, coconut is abundant since Malaysia is located at the equatorial region and has tropical rainforest climate. Coincidently, coconut grown throughout the year at the humid tropical zone. Not only that, coconut plantation rank after the palm oil tree, rubber tree and paddy in terms of the area of plantation in Malaysia. Therefore, the amount of coconut

waste accumulation in Malaysia is high. Since coconut fiber containing high cellulose content, hence it can be used to produce cellulose nanoparticles (CNPs) which can be converted into cellulose nanocomposite which has great potential in the industrial sectors. Since cellulose nanoparticles are usually being converted to nanocellulose composite in different industries, such as construction, automotive, electronics and biomedical, hence they will be subjected to many thermal degradations in many industrial processes such as composite fabrications. Therefore, it would be worth of attention to understand and predict the thermal degradation properties of the CNPs.

In this study, optimization on the extraction process was conducted in order to produce highest yield of CNPs which can then be utilized in the vast industrial-scale. Besides, the thermal degradation kinetics of the CNPs produced from the coconut fiber was studied in order to study the thermal stability as they will undergo many fabrication processes before being converted into the final consumer goods. The results of E_a are important as higher the E_a value means it will be more thermally stable and require higher amount of energy for it to be decomposed.

1.3 Objectives

The aim of this research is to optimize the CNPs production from coconut fibers and to study the thermal degradation kinetics of the produced CNPs. Therefore, this study was conducted according to the following specific objectives:

i. To optimize the production of cellulose nanoparticles (CNPs) from coconut fibers by using response surface methodology (RSM) in terms of ultrafine CNPs distribution with three factors, which are ratio of coconut fibers to ionic liquid, extraction time and extraction temperature by using the collected experimental data from the thesis of Master of Science (M.Sc.) by Nadzirah, (2014).

ii. To study the thermal degradation kinetics of the cellulose nanoparticles (CNPs) produced from coconut fiber by using the collected experimental data from the thesis of Master of Science (M.Sc.) by Nadzirah, (2014) through determination of the activation energy, E_a with the aids of two kinetic methods, which are Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) method.

CHAPTER 2 LITERATURE REVIEW

2.1 Cellulose

Cellulose is a natural biopolymer which is available abundantly in nature and can be commonly found in plant-based materials such as cotton and wood. Since cellulose is non-toxic, biodegradable and renewable, therefore the development and application of cellulose is critical to the long-term evolution of human society, particularly in the context of energy scarcity in the future. According to De Souza Lima and Borsali, (2004), around 75 – 100 billion tonnes of cellulose were produced globally in a year.

During cellulose biosynthesised, elementary fibrils will be formed and stabilized by hydrogen bonds and van der Waals forces (Boy, Narayanan and Kotek, 2017). There are two different regions within these fibrils, an amorphous region where the structure are disordered and a crystalline region where the cellulose chains are highly ordered (Rojas, Bedoya and Ciro, 2015)**.** The crystalline regions are accounted for the mechanical properties for the cellulose fibers meanwhile the amorphous regions are usually undergone degradation processes through mechanical, chemical and enzymatic processes in order to release the nanoscale components (Henriksson and Lennholm, 2009; Thomas *et al.*, 2018). These elementary fibrils are bundled to become micro-fibrils which subsequently form cellulosic fibers (Trache *et al.*, 2020)**.** Hemiacetal group and hydroxyl group are found in each of the cellulose chains. Therefore, hydrogen bonding can be formed between the hydroxyl (-OH) group in the same cellulose chain (intramolecular) and between different cellulose polymers (intermolecular) which enable the cellulose fibers to have good stiffness, high strength and good flexibility (Henriksson and Lennholm, 2009). Through mechanical, chemical or enzymatic treatments or combination of them, the cellulosic fibers can be converted into cellulose nanoparticles (Trache *et al.*, 2020).

2.2 Types of Cellulose Nanoparticles (CNPs)

There are two main types of cellulose nanoparticles, which are cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs), which mainly depends on the source of feedstocks and the extraction methods (Thomas *et al.,* 2018)**.** Cellulose nanocrystals (CNCs) are usually in rod-like, elongated and cylindrical shapes, with a length of 100 – 6000 nm and width of 4 – 70 nm (Trache *et al.*, 2020)**.** CNCs is usually produced from acid hydrolysis of cellulose fibers where a large portion of the more accessible and disordered parts, the amorphous regions are being removed (Börjesson and Westman, 2015; Thomas *et al.*, 2018)**.** Since the amorphous regions are being removed, hence the CNCs are more rigid and has a degree of crystallinity of 54 – 88 % (Thomas *et al.,* 2018)**.** Cellulose nanofibrils (CNFs) are flexible and are in entangled network structure (Thomas *et al.*, 2018; Trache *et al.*, 2020)**.** CNFs has large surface area, where they have width in the range of 20 – 100 nm and length in the range of micrometer scale (Thomas *et al.,* 2018; Trache *et al.,* 2020)**.** CNFs can be produced by mechanical, chemical, and enzymatic treatments, or a combination of these methods (Trache *et al.*, 2020)**.** Mechanical treatment is usually applied where the amorphous regions in the cellulose are preserved, causing CNFs have lower crystallinity with respect to CNCs (Thomas *et al.*, 2018; Trache *et al.*, 2020)**.**

2.3 Feedstock for CNPs Production & Coconut Fiber (CF)

Agricultural sector producing a large volume of waste annually and it is usually burnt in open fire causing air pollution or accumulated in the soil. The main composition of lignocellulosic biomass are cellulose, lignin and hemicellulose which is very suitable to be utilized for the production cellulose nanoparticles (CNPs) (Ilyas *et al.,* 2020). According to the analysis report from Food and Agricultural Organization, around 35 million tons of natural fibers are produced annually from agricultural sector by different types of animal and plants

(Ukkund *et al.*, 2018)**.** These natural fibers can be eventually used to produce valuable consumer goods. A variety of plants have been studied by researchers to produce CNPs, for example rice husk, banana peel, sugarcane bagasse, wood and coconut husk (Kargarzadeh *et al.*, 2017)**.** The following **Table 2.1** shows the cellulose composition in different types of agricultural waste.

Table 2.1 Cellulose Composition for Different Types of Natural Fiber

Natural fibers	Cellulose Composition (wt. %)	Reference
Banana peel	12.10	(Tibolla *et al.*, 2018)
Rice husk	33.43	(Abbas and Ansumali, 2010)
Wood	40.00 – 45.00	(Rowell *et al.*, 2012)
Coconut fiber	43.44	(Das *et al.*, 2016)
Sugarcane bagasse	55.81	(Samariha and Khakifirooz, 2011)

Coconut fiber is one of the possible feedstocks that can be used to produce cellulose nanoparticles (CNPs). Coconut fiber is usually extracted from the coconut husk and is removed through combing and crushing from the coconut shell. Raw coconut fiber has length of 15 – 35 cm and diameter of 50 – 300 µm. Coconut fiber are immature and is hard and yellow in colour due to the deposition of lignin layer in the cell wall. Due to the presence of lignin layer, coconut fiber has good stiffness and can be used to produce consumer goods such as mattress, upholstery and coarse filling materials. The following **Table 2.2** shows the composition of the coconut fibers.

Table 2.2 The Composition of the Coconut Fibers (Verma *et al.*, 2013)

Item	Composition (wt. %)
Water soluble	5.25
Pectin and related compounds	3.00
Hemicellulose	0.25
Lignin	45.84
Cellulose	43.44
Ash	2.22

According to the information from the International Year of Natural Fibers 2009, the main production of coconut fiber was from both India and Sri Lanka, whereby the annual production from worldwide was around 500,000 tons (Ali, 2010)**.** The main exporters for coconut fibers are India, Sri Lanka, Thailand, Vietnam, Philippines and Indonesia (Ali, 2010)**.** In Malaysia, coconut tree is another crucial industrial crop, where it is ranked after the palm oil tree, rubber tree and paddy in the aspect of the planted areas in Malaysia (Zik, Sulaiman and Jamal, 2020)**.** The plantation area of coconut tree in Malaysia is 95,000 hectares (Zik, Sulaiman and Jamal, 2020)**.** The statistic of coconut production in Malaysia is shown in **Table 2.3** below. It can be observed from the table, the production of coconut in 2017 in Malaysia was 517,589 tons. The annual coconut waste produced in Malaysia is 273,000 tons (Zakaria, Z. A., Boopathy, R., & Dib, 2020)**.** Besides, in 2007, there was 90,000,000 coconuts imported from Indonesia into Malaysia (Zik, Sulaiman and Jamal, 2020)**.** Thus, the coconut waste has been increased due to this scenario. Hence, since coconut fibers contain high amount of cellulose, therefore the widely abundant coconut in Malaysia can be made use to produce cellulose nanoparticles (CNPs) which can be further converted into valuable consumer goods.

Table 2.3 Coconut Production in Malaysia from 2012 - 2017 (Muzarpar *et al.*, 2020)

Year	Coconut Production in Malaysia (tons)
2012	624,152
2013	624,727
2014	595,097
2015	504,614
2016	504,773
2017	517,589

2.4 Production of Cellulose Nanoparticles (CNPs) from Agricultural Waste

There are several types of pretreatments and extraction methods for the CNPs production. The biomass pretreatment is important in order to remove the non-cellulosic components and the remaining cellulosic materials is ready for further CNPs extraction

(Phanthong *et al.*, 2018). The common pretreatments for biomass are alkali treatment and acid-chlorite treatment. Commonly, sodium hydroxide with 4 – 20 wt. % is used and stirred with holocellulose for 1 – 5 hours (Cullen and Macfarlane, 2005; Johar, Ahmad and Dufresne, 2012). After washing the product with distilled water until the pH value becomes neutral, the product is dried at 50 °C by using an oven (Phanthong *et al.*, 2018). This pretreatment aims to remove the amorphous polymer of hemicellulose and the remaining lignin. The delignification or bleaching process is referring to the acid-chlorite treatment. This pretreatment stirs the lignocellulosic biomass with sodium chlorite, acetic acid and distilled water at 70 – 80 °C for 4 – 12 hours (Cullen and Macfarlane, 2005; Mandal and Chakrabarty, 2011; Johar, Ahmad and Dufresne, 2012; Santos *et al.*, 2013). After the mixture pH value become neutral, the obtained white colour product, holocellulose is dried at 50 °C by using an oven (Phanthong *et al.*, 2018). The objective of this pretreatment is to remove most of the lignin and impurities.

There are several types of developed extraction method for CNPs from cellulosic materials and the types and properties of CNPs are dependent on the extraction method. The three main extraction methods for CNPs are enzymatic hydrolysis, acidic hydrolysis and mechanical treatment. Acid hydrolysis is commonly used because the acid can hydrolyze the disordered region in the cellulose chains easily to isolate the CNPs and maintain the ordered region (Moon *et al.*, 2011; Lavoine *et al.*, 2012). Sulfuric acid is usually used because the presence of sulfate ions can help in esterification of hydroxyl group which in turn making the CNPs become a stable colloid system (Bondeson, Mathew and Oksman, 2006; Lu and Hsieh, 2010). For acidic hydrolysis, the main controlling factors for CNPs extraction are extraction time, acid concentration and the reaction temperature (Lavoine *et al.*, 2012). Washing process which is used to neutralize the pH value the produced CNPs suspension in the acidic hydrolysis causing the main drawback for this method as it produces large amount of acidic wastewater. The washing process can be done by using cold water followed by centrifugation process or by

using alkaline such as sodium hydroxide (Wang, Ding and Cheng, 2007; Johar, Ahmad and Dufresne, 2012). Besides that, CNPs can be extracted by using a biological method, which is enzymatic hydrolysis whereby the cellulose fibers will be digested or modified by the enzymes (Abdul Khalil *et al.*, 2014). Enzymatic hydrolysis has the advantage of milder reaction conditions; but this causes the process operation time becomes longer (Moniruzzaman and Ono, 2013; Abdul Khalil *et al.*, 2014). Hence, usually other methods are incorporated with enzymatic hydrolysis in order to solve this issue. According to the research of Moniruzzaman and Ono (2013), ionic liquid pretreatment was applied to increase the surface accessibility of the cellulose fibers from wood chips before enzymatic hydrolysis with the enzyme laccase. The produced CNPs has higher crystallinity and better thermal stability than the raw wood fibers. Apart from that, mechanical method is also widely applied to extract CNPs from cellulosic materials by exerting strong shear force in longitudinal axis to separate the cellulose fibers (Abdul Khalil, Bhat and Ireana Yusra, 2012; Dufresne, 2012; Abdul Khalil *et al.*, 2014). The examples of mechanical methods are ball milling method, ultrasonication and high-pressure homogenization methods. For ball milling method, the CNPs are extracted by rupturing the cellulose fibrils into smaller size. When the jar is rotating, centrifugation force produces which then causing the formation of shear force between the balls and between the balls and jar surface (Baheti, Abbasi and Militky, 2012; Barakat *et al.*, 2014). For ultrasonication method, the hydrodynamic forces of ultrasound is utilized to defibrillate the cellulose fibers (Dufresne, 2012). As for high pressure homogenization method, which is also known as HPH, the impact force and shear force are generated break the cellulose fibers into small size in nanometers scale when the cellulose slurry flows in the vessel under high pressure and high velocity (Abdul Khalil *et al.*, 2014). The main drawback for mechanical method would be the energy intensive issue. Therefore, the mechanical method is usually associated with other pretreatment method in order to lower down the energy consumption (Abdul Khalil *et al.*, 2014).

In the research of Santos *et al.* (2013), pineapple leaf was chosen to be the raw materials for the extraction of CNPs in order to discover the potential of pineapple leaf to be converted into CNPs. The pineapple leaf underwent the purification pretreatment through milling process and treatment with sodium hydroxide with mechanical stirring, followed by bleaching process with acetate buffer and aqueous sodium chlorite. The diluted alkali pretreatment was mainly aimed to remove the lignin, hemicellulose and other non-cellulosic components which will hinder the subsequent acidic hydrolysis while bleaching process was applied to remove the remaining lignin. Acidic hydrolysis extraction method of CNPs was applied by sulfuric acid to disintegrate the amorphous regions in the cellulose and forming well-defined crystals. Through esterification of the hydroxyl groups (-OH) in the cellulose of pineapple leaf, the sulfate groups from the sulfuric acid were introduced to the surface of the cellulose nanoparticles. This allowed the stable aqueous dispersion of CNPs due to the anionic stabilization resulted from the repulsive forces. The results obtained showed that increasing in reaction time would lead to decrease in the dimensions of CNPs. The experimental results showed that the best reaction time was 30 mins. The produced CNPs have the characteristics of high thermal stability at 225 °C, high crystallinity of 73 %, in needle-shaped and having L/D ratio around 60 (length: 249.7 ± 51.5 nm, diameter: 4.45 ± 1.41 nm).

In the study of Ramesh and Radhakrishnan (2019), CNPs were extracted from potato peel to be incorporated with polyvinyl alcohol (PVA) based film. The potato peel first undergone alkali pretreatment by using sodium hydroxide and bleaching process. The extraction method of CNPs was the combination of acidic hydrolysis by using sulfuric acid and high-pressure homogenization. The experimental results showed a CNPs yield of 39.8 ± 0.5% from potato peel. By using transmission electron microscopy (TEM), needle-shaped CNPs were observed with a width range of 100 – 200 nm. The CNPs also showed high crystallinity of 86.21 % and major diffraction peaks of 34.81°. The results also showed that the CNPs

produced was suitable to be incorporated to the packaging film to increase the film property by increasing the tensile strength, elongation property and thermal stability.

As for Purkait *et al.* (2011), they have done the research of CNPs extraction from sesame husk. Firstly, delignification process and alkali treatment were done to remove the lignin and hemicellulose and non-cellulosic content. The extraction of CNPs from pretreated sesame husk involves acidic hydrolysis, centrifugation, high pressure homogenization and ultrasonication. The CNPs produced was observed to be in spherical shape and the diameter was in the range of 30 – 120 nm. Problem faced during the drying of CNPs due to the strong reaggregate tendency of the cellulose and partially lost nanosize effect.

Extraction of CNPs from banana peel was studied by Tibolla, Pelissari and Menegalli (2014) in their research. Both the acidic hydrolysis and enzymatic hydrolysis were utilized to extract CNPs from banana peel. Based on the appearance of the CNPs suspension at the end of extraction, white material emerged for the acidic hydrolysis while light yellowish pulp (not totally white) emerged for the enzymatic extraction. This was due to acidic hydrolysis can completely delignify the cellulose and dissolve the hemicellulose, while enzymatic extraction can only complete it partially. Due to this issue, the xylanase enzyme cannot penetrate the cellulose chains, causing low cellulose hydrolysis efficiency. The obtained CNPs yield from acidic hydrolysis was 5.1 %, which was lower than the enzymatic hydrolysis (10 %). The CNPs from acidic hydrolysis has diameter and length of 10.9 ± 2.3 nm and 454.9 ± 6.6 nm, meanwhile the CNPs from enzymatic hydrolysis has diameter and length of 7.6 ± 1.5 nm and 2889.7 ± 241.3 nm, respectively. Besides, the crystallinity of CNPs produced from acidic hydrolysis (58.6 %) was higher than enzymatic hydrolysis (49.2 %), this was due to the acidic hydrolysis extraction posed greater amorphous region ability than the enzymatic extraction.

Generally, the production of cellulose nanoparticles (CNPs) from coconut fiber involves two steps, where the first step is the coconut fiber fractioning and the second step is the main cellulose nanocrystals (CNCs) extraction. In the first step, the coconut fiber undergoes size reduction through mechanical grinding, delignification and also bleaching processes. The delignification and bleaching process are vital because it helps to reduce the lignin and hemicellulose contents, enabling more cellulose to be extracted. According to the research from Nascimento *et al.*, (2016), two acidic hydrolysis extraction conditions were used to extract CNPs from the coconut fibers, where the first one was in low sulfuric acid concentration (44 % w/w), longer reaction time (360 mins) and higher temperature (60 °C), meanwhile the second condition was in higher sulfuric acid concentration (60 % w/w), shorter reaction time (45 mins) and lower temperature (60 °C). Out of expectation, the milder hydrolysis condition, which was the first condition with higher acidic concentration, resulted a higher yield (59.8 ± 2.1 %) than the second condition (32.8 ± 0.2 %). This can be explained as the harsher extraction conditions have higher acid concentrations, which even broke the crystalline region in the cellulose structure into oligo and monosaccharides, leading towards low CNPs level and low overall yield (Chenampulli *et al.*, 2013). Both the acidic hydrolysis extraction resulted CNPs in needle-shaped and well dispersed, however the length and width of CNPs were different. The first condition resulted CNPs with length of 128 ± 52 nm and width of 6.6 ± 1.5 nm, meanwhile the harsher condition resulted CNPs with length and width of 208 ± 34 nm and 4.9 ± 0.5 nm, respectively. Besides, the CNPs produced from harsher condition also resulted in higher crystallinity (80 %) than the first condition (79 %) by using Segal approach.

In the research of Nascimento *et al.*, (2014), cellulose nanowhiskers (CNWs) was extracted from the unripe coconut husk fibers. Organosolv process was first used to delignify the coconut husk fibers, then proceeded with the alkaline bleaching and acidic hydrolysis extraction with 30 % (v/v) of sulfuric acid at 60 °C for 360 mins. Under these conditions, the

CNWs produced have an average length of 172 ± 88 nm and diameter of 8 ± 3 nm. Besides, it was concluded that organosolv pulping process has better lignin removal efficiency than the chlorine pulping process and using lower acid concentration during extraction process was important as for the green chemistry aspect.

According to the research of Rosa *et al.*, (2010), cellulose nanowhiskers (CNWs) were extracted from coconut fiber and the effect of preparation on the thermal and morphological behavior of the CNWs were studied. The results showed that under milder condition of bleaching process, the produced CNWs has better thermal performances due to the presence of the residual lignin. Also, with lower hydrolysis time (120 mins), the CNWs have better aspect ratio, with an average length of 190 ± 70 nm and width of 5.5 ± 1.5 nm as longer hydrolysis time could results in partial dissolve in crystalline region which eventually caused shortening in the length of CNWs.

There were also many researches regarding the incorporation of CNPs from coconut fibers into the biodegradable films and nanocomposites. In the research of Wu *et al.*, (2019), CNPs with average diameter of 5.6 ± 1.5 nm were extracted from coconut fibers. The CNPs were then incorporated with the polyvinyl alcohol (PVA) to form CNF/PVA composite films, where the results showed that the incorporation of CNF into PVA successfully reinforced major properties of the PVA films. Meanwhile, in the study of Bruna *et al.*, (2017), they extracted CNPs from coconut fiber by using sulfuric acid hydrolysis with the conditions of 10 – 15 mins of extraction time, 50 °C of extraction temperature and acid concentration of 64 % v/v. The CNPs then incorporated to the cassava starch films plasticized with glycerol and the results showed that the mechanical properties of films such as Young's modulus and maximum tension have been significantly improved. **Table 2.4** below shows the summary of production of CNPs from agricultural waste.

Table 2.4 Summary of Production of CNPs from Agricultural Waste

Fibers	Pretreatment	Extraction Method	CNPs Characteristic	Reference
Pineapple leaf	Milling Alkali treatment Bleaching	Acidic hydrolysis (H_2SO_4)	Needle-shaped L = 249.7 ± 51.5 nm D = 4.45 ± 1.41 nm Crystallinity = 73 %	(Santos *et al.*, 2013)
Potato peel	Alkali treatment Bleaching	Acidic hydrolysis (H_2SO_4)	Needle-shaped W = 100 – 200 nm Crystallinity = 86.21 %	(Ramesh and Radhakrishnan, 2019)
Sesame husk	Delignification Alkali treatment	Acidic hydrolysis (H_2SO_4) Centrifugation HPH	Spherical-shaped D = 30 – 120 nm	(Purkait *et al.*, 2011)
Banana peel	Alkali treatment Delignification	Acidic hydrolysis (H_2SO_4) Centrifugation	L = 454.9 ± 6.6 nm D = 10.9 ± 2.3 nm Crystallinity = 58.6 %	(Tibolla, Pelissari and Menegalli, 2014)
Banana peel	Delignification Centrifugation	Enzymatic hydrolysis (xylanase)	L = 2889.7 ± 241.3 nm D = 7.6 ± 1.5 nm Crystallinity = 49.2 %	
Coconut fiber	Grinding Delignification Bleaching	Acidic hydrolysis (H_2SO_4) **[1 & 2]**	**[1]** Needle-shaped L = 128 ± 52 nm W = 6.6 ± 1.5 nm Crystallinity = 79 % **[2]** Needle-shaped L = 208 ± 34 nm W = 4.9 ± 0.5 nm Crystallinity = 80 %	(Nascimento *et al.*, 2016)
Unripe coconut husk fiber	Acetosolv pulping Alkaline bleaching	Acidic hydrolysis (H_2SO_4) Ultrasonication	Needle-shaped L = 172 ± 88 nm D = 8 ± 3 nm Crystallinity = 82 %	(Nascimento *et al.*, 2014)
Coconut husk fiber	Milling Alkaline treatment Bleaching	Acidic hydrolysis (H_2SO_4) Centrifugation	L = 190 ± 70 nm W = 5.5 ± 1.5 nm Crystallinity = 65.9 ± 0.2 %	(Rosa *et al.*, 2010)

2.5 Ionic Liquids (ILs) Extraction of CNPs

Ionic liquids are organic solutions which consist of cations and anions and it can stay in fluid state at temperature under 100 °C (Xie *et al.*, 2018). The ILs extraction method is

gaining the interests due to advantages posed by the ILs, which are good chemical and thermal stability, non-flammable and very low vapour pressure (Zhu *et al.*, 2006; Pinkert *et al.*, 2009). The utilization of ILs meets two green chemistry principles, which are using environmentally-friendly solvents and using bio-renewable source (Kargarzadeh *et al.*, 2017). Some of the examples of ILs are 1-allyl-1-methylimidazolium chloride (AmimCl), 1-butyl-3-methylimidazolium chloride (BmimCl), 1-butyl-3-methylimidazolium hydrogen sulphate ($BmimHSO_4$) and 1-butyl-3-methylimidazolium acetate (BmimoAc). The ILs can swell, dissolve and hydrolyse the cellulose and convert it into valuable chemicals and products. The mechanisms of cellulose dissolution of ILs consist of two steps, where cations from the ILs attack the oxygen atom in the cellulose, meanwhile the anions from the ILs associate with the protons of the hydroxyl groups in the cellulose chains (Kargarzadeh *et al.*, 2017). With these two interactions, the hydrogen bond networks in the cellulose chains can be broken down, leading to dissolution of cellulose (Kargarzadeh *et al.*, 2017). ILs has high potential to extract CNPs as it will not be consumed during the reaction and can be recovered for further reused. The main disadvantage of ILs is high cost and contains some toxicity. Hence, further researches are required to develop ILs which are highly efficient, safe to be used and cheap in price.

In the research of Li *et al.*, (2012), CNPs were extracted from the sugarcane bagasse with ILs extraction with BmimCl as the ionic liquid. With the condition of dissolution temperature of 130 °C, cellulose concentration in IL solution of 1 wt. % and microwave power of 400 W, good solubilization of cellulose was observed. According to the research of Man *et al.*, (2011), $BmimHSO_4$ was used to extract CNPs from the microcrystalline solution. The IL broke the hydrogen bonds between the cellulose chains and produced needle-like CNPs with length of 50 – 300 nm and diameters of 14 – 22 nm. Also, in the study of Tan, Abd Hamid and Lai, (2015), high recovery yield of CNPs (more than 90 %) was obtained in the research of by using ILs extraction with $BmimHSO_4$. In addition, by using tetrabutylammonium acetate

(TBAA) ionic liquid, CNPs with width of 20 – 30 nm were produced from the wood pulp board (Miao *et al.*, 2016). In the research of Chen *et al.*, (2011), the results showed that by increasing the dissolution temperature, the crystallinity of the CNPs increased due to the removal of lignin and hemicellulose components in the amorphous region. It was concluded that ILs are more selective in removing the amorphous region and help in the growth and realignment of monocrystals.

2.5.1 Affecting Factor for Cellulose Nanoparticles (CNPs) Extraction

There are few depending factors on the CNPs extraction from cellulosic materials depending on the type of extraction method. Since the collected data for CNPs extraction was ionic liquid extraction-based, hence the relating factors will be discussed. The general factors which might affect the morphology, crystallinity and thermal stability of the extracted CNPs are the reaction conditions such as reaction temperature, time and also ratio of substrate to ionic liquid.

2.5.1(a) Reaction Temperature

In the research of Samsudin *et al.* (2020), the CNPs were extracted from microcrystalline cellulose by using ionic-liquid extraction method, with 1-butyl-3-methylimidazolium acetate (BmimOAc) as a catalyst and solvent under different sets of temperature which ranged from 70 – 110 °C with 10 °C of interval. The experimental results showed that the diameter of the CNPs produced increased as the temperature increased. The CNPs experienced structural disruption at temperature higher than 100 °C, particularly at 110 °C. This was mainly due to the enlargement of the existing porous structure and also texture alteration when the synthesis process occurred at high temperature (100 °C). As for the crystallinity, the crystallinity of CNPs produced decreased from 59.4° – 39.2° when the temperature increased from 70 – 110 °C. At low temperature, the weak van der Waals force within the amorphous region can be easily overcome, meanwhile at high temperature, the

strong hydrogen-bonding in the crystalline region is being ruptured (Mohammad Mohkami and Mohammad Talaeipour, 2011).

2.5.1(b) Reaction Time

In the study of Wang *et al.* (2011), cellulose was extracted from pine, poplar, Chinese parasol, and catalpa wood chips by using ionic liquid extraction method. The ionic liquid used was 1-allyl-3-methylimidazolium chloride (AmimCl). The extraction rate of cellulose increased as the dissolution time increased for all kind of wood samples except for catalpa. By taking the pine wood as example, the extraction rate increased from 16 % to 26 % when the dissolution time increased from 3 to 24 hours.

2.5.1(c) Weight Concentration of Substrate to Ionic Liquid

Also, in the study of Wang *et al.* (2011), the initial concentration of wood to the ionic liquid was also taken into consideration. According to the experimental results, the extraction rates favored low weight concentration of wood, whereby the extraction rate decreased from 35 % to 26 % when the initial wood concentration increased from 1 to 5 wt. %. This might be due to dispersion of molecules in the ionic liquid solution at low concentration which in turn increases the extraction rate.

2.6 Optimization on the Production of Cellulose Nanoparticles (CNPs)

Response surface methodology (RSM) is used to develop functional relationship between the manipulated or controlled variables and the interested responses by using mathematical and statistical analysis (Khuri and Mukhopadhyay, 2010). The relationship between the variables and response are unknown but it can be solved by fitting them into a low-degree polynomial model. The aim of using RSM is to achieve process optimization and the main objectives are to build up a relationship between variables and responses for future prediction of response for given variables value, to find out the significance of each of the

manipulated variables and to discover the optimum settings for the variables for maximum responses (Khuri and Mukhopadhyay, 2010). Before conducting RSM, a number of experiments need to be conducted to obtain the response over different settings of variables. The sum total of these settings will be constructed in matrix, which is known as the surface response design (Khuri and Mukhopadhyay, 2010). The matrix has to be fitted nicely to assure the quality of the prediction whereby minimum variance can be achieved. For first-degree model, 2^k Factorial Design, Plackett–Burman Design and Simplex Design are commonly used. For second-degree model, 3^k Factorial Design, Central Composite Design (CCD) and Box-Behnken Design are usually applied. Both the CCD and Box-Behnken methods are popular and are fitted accordingly to the type of experiment. Both methods examine the factor on 3 levels and also have the same mathematical model (Rakić *et al.*, 2014). The main difference between these two methods is the number of experiment requirement, whereby CCD require more number of experiment than Box-Behnken method (Rakić *et al.*, 2014). Besides, CCD also takes into account for the combinations of extreme factors, however Box-Behnken does not examine the borderline regions (Rakić *et al.*, 2014). In addition, CCD is simple and effective as it not only consists of orthogonal factorial points and center points, it also augmented with axial points which are two points selected from the axis of the variables with a distance of α from the design center (Montgomery, 2006; Khuri and Mukhopadhyay, 2010). Face-centered CCD design with $\alpha = 1$ was used as only three levels for each variables and 2 – 3 center points are required in order to provide a good variance prediction throughout the experimental design (Montgomery, 2006).

The information and results for the optimization for CNPs production from coconut fiber is lacking of, therefore the results of optimization based on other types of feedstocks are being reviewed. In the research of Meyabadi and Dadashian (2012), the CNPs were extracted from waste cotton fibers by using enzymatic hydrolysis. Optimization process was done by

using RSM with Box-Behnken Design. The particle size was chosen to be the response, meanwhile the manipulating factors were hydrolysis time, substrate concentration and enzyme loadings. 15 runs of experiment with 3 factors on 3 levels and also 3 replicates on center point were used to model the optimization process. By using the contour plot and analyzing the response surface, the obtained optimum operating settings i.e. enzyme loadings, hydrolysis time and substrate concentration were 2.3 %, 175 h, 5 g/l, respectively. By extracting the CNPs under these optimum conditions, the CNPs were in spherical-shaped and the size ranged from 40 – 90 nm.

In the research of Vanderfleet, Osorio and Cranston (2018), CNPs were extracted from cotton by using acidic hydrolysis (phosphoric acid). The manipulating factors were temperature, hydrolysis time and acid concentration, meanwhile the output responses were CNPs length, phosphate content and zeta potential. 3^k Factorial Design was used to model the optimization process, hence a total of 9 run of experiments were done, which were 8 sets of experimental results and one central point with condition (0,0,0). Based on the results from optimization process, the temperature and acid concentration have greatest impact on the CNPs length, whereby increasing in both the factors resulted in small CNPs size with shorter length. For phosphoric content, both the hydrolysis time and temperature showed greater impacts, meanwhile there was negligible effect on zeta potential while manipulating the hydrolysis parameters.

In the research of Thakur *et al.*, (2020), the cellulose nanocrystals was produced by using rice straw as the feedstock. By doing optimization with response surface methodology (RSM) with CCD method, a total of 20 runs of experimental results were done. The three selected factors were acid concentration, reaction temperature and reaction time, meanwhile the response of optimization was the production yield. The highest yield of production was

90.28 % when the reaction conditions were temperature at 30 °C, sulphuric acid concentration of 75 wt. % and reaction time of 5 hours.

In the research of Hemmati, Jafari and Taheri, (2019), combination of acidic hydrolysis and homogenization-ultrasonication method was used to extract cellulose nanocrystals from cotton linter. The CNC production was optimized under a 3-factor and 3-level FCCD design. The affecting factors being selected were the homogenization speed, hydrolysis time and also acid concentration. A maximum CNC yield of 59 % was obtained from the optimization results from Design Expert software under the reaction conditions of 4.5 mins of hydrolysis time, 9000 rpm of homogenization speed and 5.9 % of acid concentration.

In the research of Chowdhury *et al.*, (2019), cellulose nanowhiskers (CNW) was extracted from the leaves of *Adansonia kilima* (AK) by using ILs extraction with $BmimHSO_4$ as the ionic liquid along with the ultrasonication. The process parameters chosen were the hydrolysis time, hydrolysis temperature and ultrasonication power. Meanwhile, the response selected was the CNW crystallinity index and CNW yield. A two-level factorial Box-Behnken Design (BBD) was utilized to carry out the optimization process in Design Expert software. The optimized results were crystallinity index of 87.88 % and yield of 85.29 %, under 200 watts of ultrasonication power, 43.11 mins of hydrolysis time and 94 °C of hydrolysis temperature. **Table 2.5** below shows the summary of optimization of production of CNPs.

Table 2.5 Summary of Optimization of Production of CNPs

Natural fiber	Optimization Design	Affecting Parameter	Response	Reference
Waste cotton	Box-Behnken Design (BBD)	Enzyme loading Hydrolysis time Substrate concentration	Particle size	(Meyabadi and Dadashian, 2012)
Cotton	3^k Factorial Design	Acid concentration Hydrolysis temperature Hydrolysis time	CNPs length Phosphate content Zeta potential	(Vanderfleet, Osorio and Cranston, 2018)
Rice straw	Central-Composite Design (CCD)	Acid concentration Reaction temperature Reaction time	Production yield	(Thakur *et al.*, 2020)
Cotton linter	Face-Centered Composite Design (FCCD)	Hydrolysis time Homogenization speed Acid concentration	Production Yield	(Hemmati, Jafari and Taheri, 2019)
Leaves of *Adansonia kilima* (AK)	Box-Behnken Design (BBD)	Ultrasonication power Hydrolysis time Hydrolysis temperature	CNWs crystallinity CNWs yield	(Chowdhury *et al.*, 2019)

2.7 Thermal Degradation Kinetics of the Cellulose Nanoparticles (CNPs)

Thermogravimetric analysis (TGA) is known as a method to measure the changes in mass of a sample while varying the temperature (Vyazovkin, 2012). This analysis can be done isothermally by keeping constant heating rates or non-isothermally. When the sample is subjected to temperature change, it will experience gaining or losing of weight. As for CNPs, it will experience in weight loss during degradation/decomposition. Both integral and differential forms of TGA can be presented. For integral form, the mass is plotted against temperature or time, meanwhile for differential form, the derivative of TGA curve will be plotted against temperature or time (Vyazovkin, 2012). For differential TGA, mass loss or mass gain can be observed at the downward or upward peak, respectively (Vyazovkin, 2012).

In this project, the thermal degradation kinetics of CNPs will be studied by determining the activation energy, E_a of the CNPs produced from coconut fiber through two kinetic methods, which are Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) method. The thermal degradation kinetics can be studied by using both model-fitting and model-free method (Alwani *et al.*, 2014)**.** However, model-free isoconversional and multi-heating methods are more preferred due to its simplicity and avoiding the consequences of choosing the wrong kinetic model and hence getting wrong results for the kinetic parameters (Alwani *et al.*, 2014)**.** Kissinger-Akahira-Sunose (KAS) is an integral isoconversional method, which was modified based on the Kissinger equation (Svoboda, 2014). It took into consideration on the dependency of activation energy on the degree of conversion (Svoboda, 2014). For the isoconversional integral FWO method, if the reaction mechanism does not change over a range of conversion or temperature, then this method is valid at different heating rates (Dahiya *et al.*, 2008). **Table 2.6** shows the equations for the respective thermal degradation kinetics method.

By plotting a linear graph according to the equations for the respective methods in **Table 2.6**, the activation energy can be determined by finding out the gradient and y-intercept of the graphs. The results of E_a are important as higher E_a value means it will be more thermally stable and require higher amount of energy for it to be decomposed. Particularly, FWO is the most widely used method for lignocellulosic fibers by other researchers (Borsoi *et al.*, 2016). In the study of Borsoi *et al.* (2016), the thermal degradation behaviour of CNPs by using FWO kinetic model. For conversions from 0.2 to 0.8, the cellulose nanofibers (CNF) have greater average activation energy than cellulose nanowhiskers (CNW), which were 151.73 ± 6.20 kJ/mol and 151.07 ± 14.78 kJ/mol.

Table 2.6 The Equation for Respective Kinetic Method

Kinetic Method	Equation	Reference
Kissinger-Akahira-Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a[g(\alpha)]}\right) - \frac{E_a}{RT}$	(Heydari, Rahman and Gupta, 2015)
Flynn-Wall-Ozawa (FWO)	$\log(\beta) = \log\left(\frac{AE_a}{R[g(\alpha)]}\right) - 2.315 - 0.4567\frac{E_a}{RT}$	(Flynn and Wall, 1966)

* β = constant heating rate
$g(\alpha)$ = integral reaction model
T = absolute temperature
R = gas constant
E_a = activation energy
A = pre-exponential factor