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CNC (Cellulose Nanocrystals) IsolationfromVarious Agricultureand Industrial WasteUsing Acid Hydrolysis Methods

Fauzan Ahmad Zuliat, Muslim Suardi, Akmal Djamaan*
Faculty of Pharmacy, Universitas Andalas, Padang 25163, West Sumatra, Indonesia

Corresponding author: akmaldjamaan@phar.unand.ac.id

Abstract
Background: *Cellulose is the main constituent that forms the plant cell wall. The abundant content of cellulose makes cellulose very potential to be developed, the widely invented is the production of cellulose nanocrystals (CNC). The production of small cellulose such as micro or nano allows cellulose to have good stability and affinity, so that it can be used more effectively. The ideal utilization of cellulose nanocrystals (CNC) has spread in various sectors, such as water treatment, absorbents, cosmetic products, coatings, fillers, adhesives, nanocomposites, energy and electronics, biomedicine, drug additives, and includethe manufacture of other biomaterials. Therefore, it is necessary to summarize the results of cellulose nanocrystals (CNC) from various cellulose sources, especially from agriculture and industrial waste. So that further researchers can use this as reading material so that the research can be carried out optimally and efficiently by continuing what is available.*
Methods: *The method in this study is a systematic review by literature searches in the form of published journals, proceedings,and theses. Literature searches are carried out both manually (library) and electronically with the help of reputable journal search sites such as Science Direct, Research Gate, Google Scholar, and Scopus. The literature used focuses on English and Indonesian literature with publication years between 2010 until 2020. For journals used are Scopus and or SINTA indexed journals, with the keywords CNC, Cellulose Nanocrystals, nanocrystal cellulose isolation, cellulose nanocrystal agriculture.*
Results: *Several studies conducted in the manufacture of CNC using strong acids such as H_2SO4 and HCl, the summarizedresults found that there were differences in the results of CNC manufacturing based on cellulose sources and chemical and mechanical pretreatments.*
Conclusion: *Production CNC for a mass production scale requires further research to obtain optimization for each type of sample and treatment.*
Key Words:*Nanocrystalline, cellulose, nanocrystal, agriculture, industry, acid*

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I. Introduction

Cellulose nanocrystals (CNC) is a cellulose-derived polymer with a diameter of 2-20 nm and a length of 100 nm to several micrometers. Cellulose nanocrystals are also part of nanocellulose. Nanocellulose consists of three groups, 1) cellulose nanocrystals (CNC), cellulose nanowhiskers, and microcrystalline cellulose (MCC), 2) cellulose nano-fibrils (CNF), cellulose microfibrils (CMF), and 3) bacterial cellulose (BC), or also called microbial cellulose (MC)[1].

Since CNC is a natural material, it is found widely in various characteristics, sizes, degrees of crystallization, rheology, specific surface area, solubility, and stability[1].Crystalline groups in cellulose are obtained by utilizing the properties of amorphous group which have smaller density values in cellulose, this makes stong acidsable to separate amorphous groups from CNC[2].The properties of these amorphous groups allows CNC to be obtained chemically and enzymatically[3].

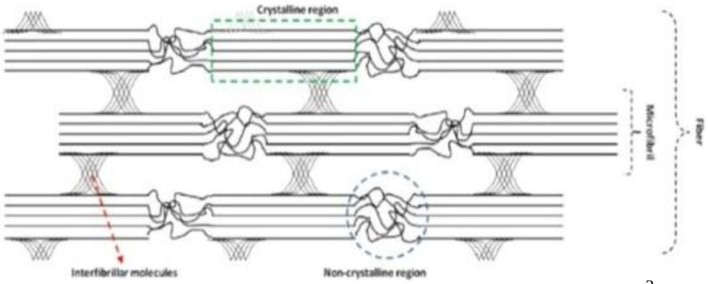


Fig.1. Crystalline and amorphous groups on cellulose[3].

Cellulose nanocrystals (CNC) are natural material that can be applied in several different application fields. CNC is widely applied in the paper industry and pharmaceutical fields. Cellulose nanocrystals have been researched and various modifications have been made. Simple chemical modification of the cellulose surface causes the nanocellulose to experience dispersability in different solvents. The Cellulose obtained from the isolation process is then hydrolyzed into nanocellulose by the acid method using strong acids[4].

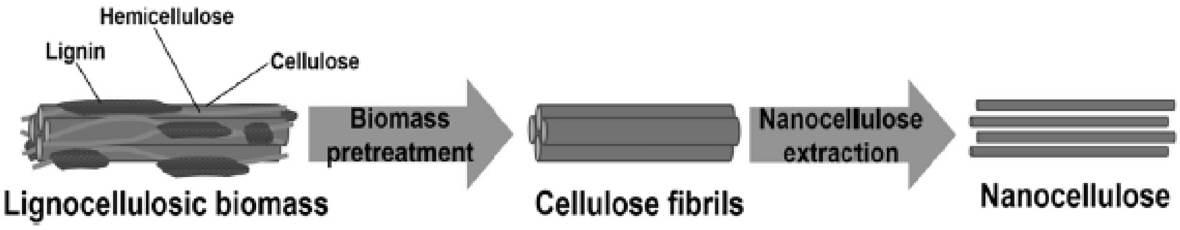


Fig.2.Schematic of nanocellulose extraction from lignocellulosic biomass[5].

II. Materials and Methods

The method in this study is a systematic review with literature searches in the form of published journals, proceedings, and theses. Literature searches are carried out both manually (library) and electronically with the help of reputable journal search sites such as Science Direct, Research Gate, Google Scholar, and Scopus. The literature used focuses on English and Indonesian literature with publication years between 2010 and 2020. For journals used are Scopus and or SINTA indexed journals, with the keywords CNC, Cellulose Nanocrystals, nanocrystal cellulose isolation, cellulose nanocrystal agriculture.

III. Results

Cellulose is an important and common natural polymer, so that cellulose occupies an important position in the advancement of human civilization today. Therefore, cellulose has enormous opportunities in various fields. With the development of science, it is very possible that cellulose can be used as the main material in the modern pharmaceutical industries,cosmetics, material industries, and other sectors. The main source of cellulose is found in plants, namely as the main constituent of plant cell walls. Cellulose derived from plants still binds to lignin in the form of ligonocellulose,Fig4.Main components **of lignocellulosic biomass: cellulose, hemicellulose, and lignin**[7]**.**

In addition, cellulose is still covered by hemicellulose. For that we need an isolation process to get pure cellulose**Error! Reference source not found.**[6].

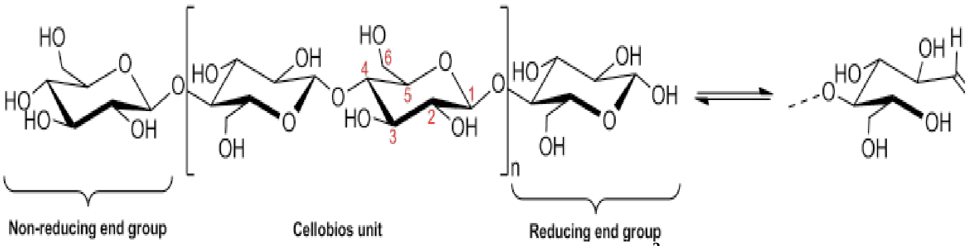


Fig.3. Chemical structure of cellulose[3]**.**

Cellulose Structure

Cellulose is a natural biopolymer of glucose monomers which are abundant on earth as the main components of plant biomass. Cellulose is a linear homopolysaccharide with the chemical formula $(C_6H_{10}O_5)_n$ where the degree of polymerization (DP) of wood is 10,000, while bacterial cellulose has a DP arround 8,000.

Cellulose polymerconsists of several D-anhydroglucopyranose units (AGU) which are bound by β-1,4-glycosidic bonds. Each D-anhydroglucopyranose (AGU) has three hydroxyl groups. These hydroxyl groups have different alcohol groups depending on their location on the chemical structure of cellulose. The hydroxyl groups at C2 and C3 positions are secondary alcohols, while the C6 hydroxyl group is the primary alcohol positions,Fig.3. These hydroxyl groups are all possible sites for chemical modification. Meanwhile, the most chemically reactive hydroxyl group is at position C6[3].

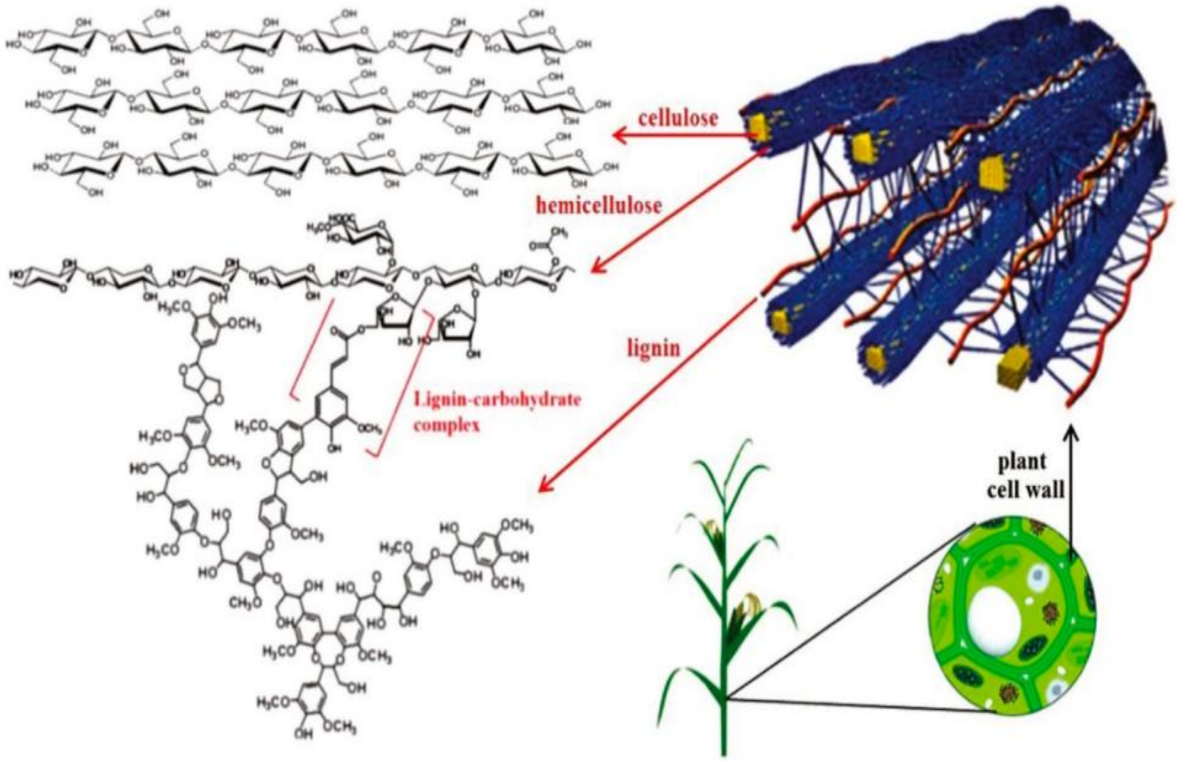


Fig4.Main components of lignocellulosic biomass: cellulose, hemicellulose, and lignin[7].

Cellulose Nanocrystals (CNC)

Cellulose Nanocrystals (CNC), are crystalline nanoparticle made of cellulose with a width of2-30 nm and 100 nm to several micrometers length.[3]The development and use of CNC is relevant to the development of environmentally friendly technologythat is developing today. Where natural and biodegradable materials are very important. Utilization of CNC in various fields such as chemistry, pharmacy, food, and medical devices[5].

Nanocellulose is cellulose with nano size. This is indicated by the increase in dispersion, biodegradability, crystallinity, aspect ratio and surface area. With the ability of these nanocelluloses, the particles of nanocellulose are used as reinforcing fillers of a polymer. Nanocellulosesare also used as additive for biodegradable products, membrane reinforcement, drug carriers and implants, and as a thickener for dispersions[8].

Source of Cellulose Nanocrystall (CNC)

Cellulose is a very abundant polymer in nature, so it can be extracted from various sources such as from plants, animals, algae, fungi, bacteria and minerals. Here are some sources of cellulose nanocrystall that have been researched and found in the agriculture and industrial waste.

Table1. Isolation of CNC from bagasse.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yields (%)	CrI (%)	
3,5%HNO_3	90	120	50%H_2SO_4	45	30	-	-	42,65	9
3,5%NaOCl	-	10							
17,5%NaOH	80	30							
5%NaOH	80	180	21.000 rpm blender	-	10	-	-	83,75	10
H_2O_2 + NaOH	80	60							
5% NaOH +	55	90	11% H_2SO_4	60	60	40,35	36,5	-	11

11% H_2O_2									
2N KOH	80	60	1 N HCl	80	120	-	44,5	-	[12]
15% H_2O_2	80	60							

Table2. Isolation of CNC from rice straw.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yields (%)	CrI (%)	
3,5%HNO_2	90	120	2,5 N HCl	100	60	56,39	54,54	-	[13]
2%NaOH + 2% $NaSO_4$	50	60							
3,5%NaOCl+17,5%NaOH	80	30							
3,5% HNO_2	90	120	2,5 N HCl	100	15	42	36,12	78	[14]
2%NaOH+2%$NaSO_4$	50	60							
3,5%NaOCl+17,5%NaOH	80	30							
7,5%NaOH	24	1440	2,5 N HCl	50	10	-	-	82	[15]
20% NaOH	80	120	64%H_2SO_4	80	15	44,5	24	-	[16]
5% H_2O_2+ 40%NaOH	80	480							
20%NaOH	80	120	2,5 N HCl	80	15	39	20,25	-	
5% H_2O_2 + 40%NaOH	80	480							

Table3. Isolation of CNC from rice husk.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yields (%)	CrI (%)	
12%NaOH	80	180	-	-	-	52,3	-	58,73	[17]
2,5%$NaOCl_2$	80	60							
4% NaOH	100	120	10 mol/L H_2SO_4	50	40	96	-	59	[18]
1,7%$HClO_2$	100	240							
3% H_2O_2	90	60	2,5 N HCl	90	15	-	13,45	-	[19]
4% NaOH	100	180	64% H_2SO_4	50	40	86	48	50	[20]
6,8% NaCl	100	240							

Table 4. Isolation of CNC from oil palm empty bunches (TKKS).

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yields (%)	CrI (%)	
17,5% NaOH	80	30	64%H_2SO_4	45	45	20,8	-	-	[21]
10% H_2O_2	80	30							
7,2% H_2O_2	55	120	64% H_2SO_4	40	45	-	18,35	-	[22]
4% NaOH	55	120							
10% NaOH	150	30	97%H_2SO_4	50	210	84,3	-	96	[23]
1% NaClO	80	60							
4% NaOH	80	180	65%H_2SO_4	45	45	81,11	-	77,8	[24]
1,7%$NaCl_2O$	80	240							
2%NaOH	50	60	48,84%H_2SO_4	45	25	42,81	24%	-	[25]
17,5%$NaOCl_2$	70	30							

Table5.Isolation of CNC from corn waste.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yields (%)	CrI (%)	
Corn Husk									
2%NaOH	60	300	10%H_2SO_4	80	360	24,87	25,9	-	[26]
2% NaOCl	80	240							
4% NaOH	80	120	64% H_2SO_4	45	60	97,6	-	68,33	[27]
1,7% NaCl	80	240							
5% NaOH	50	120	TEMPO oxidation	25	60	42,5	-	63,3	[28]
12% NaClO	25	120							
5% NaOH	28	120	60%H_2SO_4	45	120	35,3	-	92	[29]
24% H_2O_2	45	120							
2% NaOH	80	120	2%H_2SO_4	45	45	21,8	15,61	51,7	[30]

1,7% $NaOCl_2$	80	120							
NaClO + HCl	22	4320	64%H_2SO_4	45	90	-	-	83,51	31
			TEMPO	60	300	-	-	72,33	
			Ultrasonoficattion 800w		30	-	-	53,47	
Corncob									
-	-	-	55%H_2SO_4	-	-	41	14,95	-	32
NaOH	60	300	10%H_2SO_4	80	360	32,6	29,6	-	26
NaCl	80	240							
Corn Stover (Straw)									
2% NaOH	60	300	10%H_2SO_4	80	360	-	39,32	91,26	26
2% NaOCl	80	240							
1,5 g $Ca(ClO)_2$ + 10 tts AcOH	70	60	30% H_2SO_4	45	120	-	-	-	33
24% H_2O_2 + 4% NaOH	50	120	Ultrasound		8				
12% NaOH	-	-	64% H_2SO_4	45	45	-	32,4	65,2	34
$Ca(ClO)_2$ + H_2O_2	-	-							
$NaClO_2$	75	60	60% H_2SO_4	60	60	-		69,3	35
8% NaOH	80	120							
2% NaOH	80	240	55% H_2SO_4	50	15	-	62,1	43	36
1,7%$NaClO_2$	80	360							

Table6.Isolation of CNC from sawdust.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yield (%)	CrI (%)	
3% H_2O_2	90	60	HCl 2,5 N	90	15	-	22,75		19
3,8% $NaOCl_2$	50	120	80% Ethanol + Milling 200 rpm	-	120	-	-	77	37
10% NaOH+10% KOH	50	120	24 kHz Ultrasonication						
1,0 M NaOH	80	120	60% H_2SO_4 + sonikasi	60	60	-	15	90	38
2,5% NaCl	100	60							

Table7.Isolation of CNC from pineapple.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yield (%)	CrI (%)	
2% NaOH	100	240	64% H_2SO_4	45	30	-	65	73	39
1,7% NaOCl	80	240							
4% NaOH + 30%H_2O_2	70	240	50%H_2SO_4	50	60	-	67,7	92,13	40
4% KOH	80	60	20Hz Sonication	-	3				
27% NaOH + 78,8%CH_3COOH + 30%NaClO	120	60	11% $H_2C_2O_4$ + $KMnO_4$	120	15	76	69	-	41
5%NaOH	90	60	60% H_2SO_4	45	60	-	-	73	42
16%H_2O_2 + 5% NaOH	55	90							

Table 8. Isolation of CNC from paper.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yield (%)	CrI (%)	
5% NaOH	28	1440	30%H_2SO_4	45	90	-	-	36,35	43
-	-	-	64%H_2SO_4,	45	90	-	-	79,8	44
4% NaOH	125	120	45% H_2SO_4	40	20	-	45	-	45
1,7% $NaClO_2$	125	240							

5% NaOH	125	120	60% H_2SO_4	45	90	88	64,3	94,8	46
2% NaClO	125	120							
5% NaOH	125	120	65% H_2SO_4	45	60	98,7	54,6	90,15	47
2% $NaClO_2$	125	120							
2% NaOH	50	60	40% H_2SO_4	50	60	69.9±4,3	31	75,9	48
34% H_2O_2+4%NaOH	50	60							
92% CH_3COOH+ 1,4% H_2SO_4	80	180	40% H_2SO_4	50	60	64,2±5,6	24	66,9	
34% H_2O_2 + 45%NaOH	50	60							
NaOH 2%	100	180	64% H_2SO_4	45	45	97,45	-	80,15	49
NaClO 2%	70	60							

Table 9. Isolation of CNC from cotton.

Pretreatments			Treatments			Results			Ref
Methods	Temp. (°C)	Time (Min)	Methods	Temp. (°C)	Time (Min)	α-selulosa (%)	Yield (%)	CrI (%)	
-	-	-	64%, H_2SO_4	45	90	-	-	79,8	44
25% NaOH	70	60	10% H_2SO_4	70	60	-	28,74	90	50
3% NaOH + 1,5% H_2O_2	70	60							
5% NaOH	80	300	60% H_2SO_4	28	5	-	72	82	51
			9000rpm ltrasonification 350W		5				
4% NaOH	70	120	65% H_2SO_4	55	150	60	54,5	98	52
0,25% $NaClO_2$	70	120	9000rpm Ultrasonification42kHz		15				
5% NaOH	70	60	64% H_2SO_4	50	60	92	89	75	53
24% H_2O_2 + 4% NaOH	50	60							
0,1% NaClO	80	240	40% H_2SO_4	28	120	-	-	77,92	54
20% NaOH	50	240	60% H_2SO_4	60	480	-	45	-	55
			10000 rpm Sonification	-	30				

IV. Discussion

Cellulose is distributed throughout nature, found in plants, plants, animals, algae, fungi, bacteria and minerals. However, the main source of cellulose is plant fiber[4].Cellulose is a polymer which is abundant in nature, especially in plants. Cellulose is the main component of plantcellwalls[56].In the plant cell wall, there are 36 single cellulose chains connected by hydrogen bonds that connect to form basic fibers or nanocellulose. These further combine to form microfibrils 5–50 nm in diameter and several micro meters (μm) in length. These microfibrils consist of regular parts (crystalline) and irregular parts (amorphous), as shown inFig.**1**[57].

Cellulose in nature is never found in pure form, but is always bound to other polysaccharides such as lignin, pectin, hemicellulose, wax, ash and xylan. Therefore, to obtain pure cellulose, several methods are needed. Some of the methods used are mechanical methods (ultrasonic and high pressure), chemical methods (strong acid hydrolysis, organosolv, alkaline solvent, oxidation and ionic liquids) and biological method (enzymatic)[19].

Cellulose is a glucose polymerlinked by β- 1,4 glucoside bonds in a straight chain,Fig.**3. Chemical structure of cellulose[3].**

Cellulose contains about 50-90% crystalline parts and the rest amorphous parts. The β- 1,4 glucoside bonds in cellulose can be broken byacid or enzymatic hydrolysis. Complete hydrolysis of cellulose will form cellulose monomer products, namelyglucose, while incomplete hydrolysis of cellulose will produce disaccharide products from cellulose, namely cellobiose[6].

Cellulose obtained from different sources will have different polymer chain lengths. The difference in the polymer chain length will indicate different degrees of polymerization. The degree of polymerization is not only determined by the length of the polymer chain but is also influenced by the method and process of isolation. The reactivity of cellulose can be seen from the three positions of hydroxine groups on anhydroglucopyranose. The hydroxylcellulosegroupsare in the primary position and the secondary position. The hydroxylgroup in the amorphous region is more reactive so it is very easy to react. The hydroxylgroup also determines the solubility of cellulose. The presence of a hydroxyl group makes cellulose insoluble in common organic solvents and water because itformsintra and intermolecular hydrogen bonds. Cellulose can dissolve if the hydrogen bond network is broken. Cellulosecontains D-anhydroglucopyranose units (AGU)through β-glycosidic bonds which are easily broken in the presence of acid. Cellulose is semiflexible, rigid, has a high viscosity in solutions, and the ability to form fibric strands. Cellulose is solid because its structureforms intramolecular hydrogen bonds and binds to β-glucosides and the holder conformation of the D-anhydropiranose cyclic[58].

Based on the degree of polymerization (DP) and solubility of cellulose in sodium hydroxide (NaOH) 17,5%, cellulose can be divided into three types including:[59]

a. α-Cellulose (Alpha cellulose)

Cellulose is long chain cellulose, insoluble in 17.5% NaOH solution or a strong alkaline solution with DP 600-1500. α-cellulose is used as an estimator and or determinant of the purity of cellulose. Cellulose with a degree of purity α> 92% qualifies as the main raw material for the manufacture of propellants or explosives. Meanwhile, low quality cellulose is used as raw material in the paper industry and fabric industry (rayon fiber). The higher the alpha cellulose content, the better the quality of the ingredients.

b. β-Cellulose (Beta cellulose)

β-cellulose is a short-chain cellulose, dissolves in 17.5% NaOH or a strong base with a polymerization degree of 15-90, and can precipitate when neutralized. This type of cellulose dissolves easily in NaOH solution which contents17.5% at20ºC.

c. γ-Cellulose (Gamma cellulose)

γ-cellulose is the same as β-cellulose, but the degree of polymerization is less than 15 and its main content is hemicellulose . This type of cellulose dissolves easily in NaOH solution which has a contentof 17.5% at 20 ° C and will not form a precipitate after the solution isneutralized.

Cellulose has good crystallinity index and elasticity value. The safe properties of cellulose makesthis polysaccharide is widely used in various industrial fields. The industries that most utilize thecellulosesare the textile, paper, medical equipment manufacturing and cosmetics industries. Many industries engaged in the health sector usecellulose as an absorbent material for diapers and coatings. Cellulose is alsoused in biosensors to test blood sugar levels. The cellulose in the biosensorsfunctions as an additional membrane forimmobilized oxidation glucoids. This is because cellulose is elastic, which has a high tensile strength and can be penetrated by air and liquid[60].

V. CNC Isolation Method

The CNC isolation process can be divided into several types of processes, 1) mechanical, 2) chemical, 3) biological or enzymatic, 4) mixed. Most of the methods used are mixed methods, chemical-mechanical or enzymatic-mechanical. The mechanical method is basically a process of changing the size of cellulose from macro to nano in physical size, such as 1) homogenizing, 2) cyocrhusing, 3) microfluidation, 4) grinding, and 5) highintensity ultrasonication. The chemical methods used include 1) acid hydrolysis, 2) alkaline hydrolysis, 3) oxidation, 4)organosolv, and 5) liquid ionic[61].

Many chemical methods are preferred because the results obtained can be controlled by variables such as solvent concentration, reaction time and reaction temperature. In addition, chemical methods require less production time. Meanwhile, the biological method uses enzymes from bacteria or bacteria . The cellulose produced by this method has a more regular structure, low energy consumption and a lower price[61].

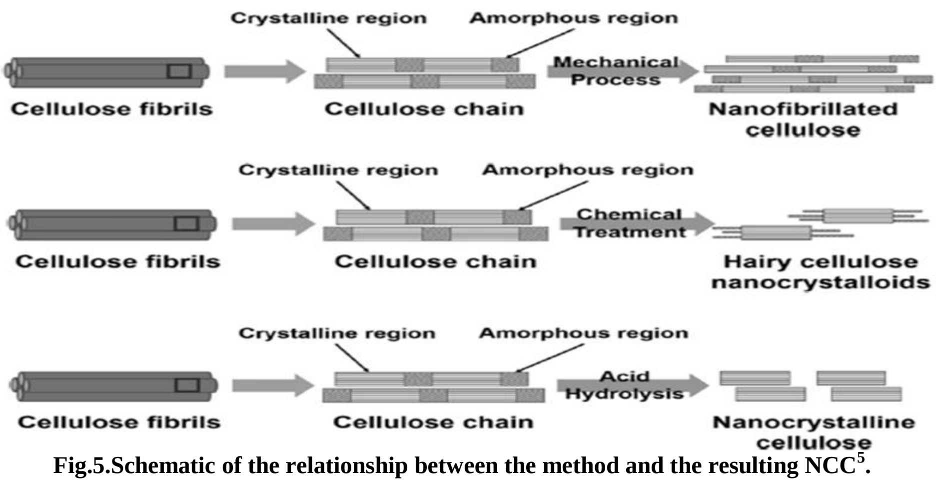


Fig.5.Schematic of the relationship between the method and the resulting NCC[5].

5.1 . Preparation

The sample to be used is washed using distilled water to remove the stuck dirt, then dry it in the sun for± 2 days. Furthermore, the dry sample was reduced in size using a grinder and then sieved using a nano filter to homogenizing the size[21].

5.2 . Pretreatment

The pretreatment process carried out to obtain pure cellulose from the sample is carried out by releasing lignin, hemicellulose and other substances from cellulose sources. The pretreatment process generally consists of delignification and bleaching. The compounds used for the pretreatment process can be alkaline compounds (NaOH, KOH, NH_4OH, and hydrazine), oxydazing agents (H_2O_2, $C_2H_4O_3$, ozone, oxygen, TEMPO, NaClO, and $NaClO_2$), organic solvents (acetone, methanol, ethanol, and ethylene glycol), and ionic liquids[61].Bagasse pretreatment using 5% NaOH and 11% H_2O_2 at 80˚C for 60 minutes produces 40,35% α-cellulose.[11] Another pretreatment to obtain cellulose from paper uses 5% NaOH and 2% $NaClO_2$ for 120 minutes at 125˚C to produce 98.7%α-cellulose[47].

For example,the pretreatment process carried out to obtain pure cellulose frombagasse sample(SCB) to release impurities. The first process was carried out usinga 0,7% (w/v) NaCl solution (ratio of sample to solution 1:50) at pH 4, adjusted with 5% acetic acid and buffer solution at pH 4. The samplewas boiled for 5 hours to remove lignin. The soaking result was washed repeatedly toneutral pHwith distilled water. Then the sample was boiled with 5% $NaSO_4$ solution for 5 hours, then washed again with distilled water to remove lignin, hemicellulose and other impurities[62].

Furthermore, the sample obtained was bleachedto remove hemicellulose completely. The sample in the form of holocellulose, was boiled in a solution of 250 mlNaOH 17,5%(w/v) for 5 hours. The yield was then filltered using Micro Filter Holder Assembly (MFHA) and washed using distilled water until the filtrate was neutral. Then, the sample was dried in open air[62].

5.3 . Treatments

The commonly used CNC preparation isthe acid hydrolysis method. This method is preferred because the results obtained can be set in according to the variables used in the treatment process. These variables are solvent concentration, reaction time, and reaction temperature.In addition, chemical methods require less production time[61]. The hydrolysis process with H_2SO_4 48.84% occurs the esterification process of cellulose hydroxyl groups with negatively charged sulfate ions on the surface of cellulose crystals. Sulfuric acid hydrolysis treatment does not change the functional groups of cellulose, but only discontinues the glucose chain[63].

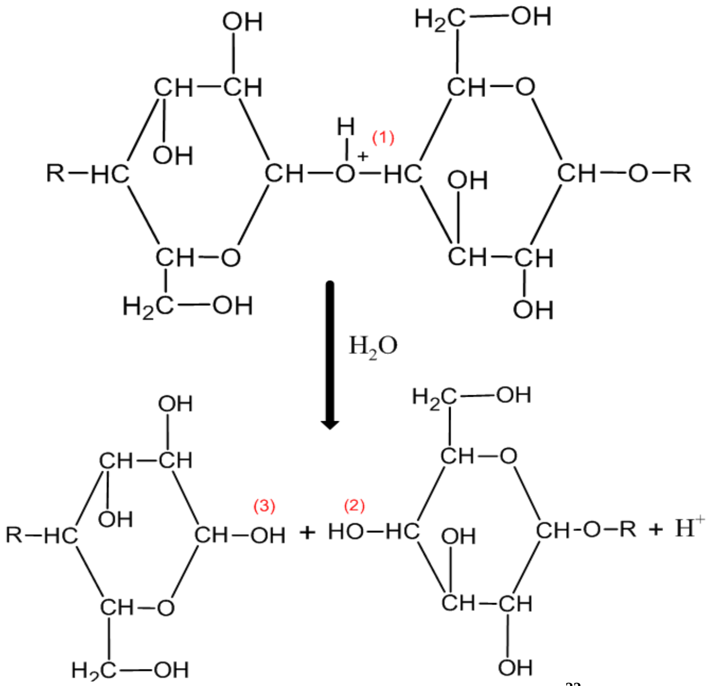


Fig.6.Acid hydrolysis reaction on cellulose [22]

For example, about 5g of cellulose is dissolved in 100 mL of 60% (w / v) sulfuric acid in a ratio of 1:20 at 45˚C for 75 min, accompanied by stirring (500 rpm). The hydrolysis solution is added with 500 mL of water to dilute the acid. After that the sample was washed with aquadest for 15 minutes and stirred at 15000 rpm. The supernatant was removed from the sediment and the water was replaced with new aquadest. The rinsing activity is carried outuntil the pH of the washing water has a pH of 7,0. Then sonification is carried out and the sample is dried to get crystals[64].

Another way to get crystals can also be done by *freeze drying* . The first sample was frozen for 24 hours and followed by *freeze drying* at 53˚C for 7 hours. The *freeze drying* process is intended to remove watercontained in nanocellulose by using the sublimation[21].

The hydrolysis scheme of cellulosic acid can be seen in Fig.6. Sulfuric acid which is diluted with water will formH_3O^+ ions, which then react with H^+ ions with one of the cellulose (1) chainsto form an OH (2) bond. This reaction producesH_2Othat reacts with other cellulose rings to form new OH bonds (3) and produce H^+ ions[22].

VI. Cellulose Nanocrystalline Characterization

Crystallinity Index

X-ray diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. X-ray diffraction is now a common technique for studying crystal structure and atomic spacing. XRD provides information about the structure, phase, orientation of the dominating crystal (texture), and other structural parameters such as mean particle size, crystallinity, stress and crystal defects. The XRD peaks are generated by the constructive interference of the monochromatic rays scattered at a certain angle from each sequence of cut fields in the sample. These X-rays are generated by the cathode tube, filtered to produce monochromatic radiation, humidifier to concentrate and directed at the sample[65].

The degree of crystallinity can be calculated by two methods, first with the general equation proposed by Wunderlich (1973), and others, as suggested by Segal *et.al* (1962) as follows: [66]

The Segal Equation :

$$\mathrm{CI_s} = \frac{\mathrm{I_{002}} - \mathrm{I_{am}}}{\mathrm{I_{002}}} x\ 100\%$$

Where :

CI_s is the degree of crystallinity using the Segalmethod

I_{002} is the intensity of cellulose crystals ($2\Theta = 22.5˚$);

I_{am} is the intensity of the amorphous cellulose group ($2\Theta = 18˚$)

The Wunderlich Equation:

$$\mathrm{CI_w} = \frac{k\mathrm{I_c}}{\mathrm{I_c} - \mathrm{I_A}} x\ 100\%$$

Where :

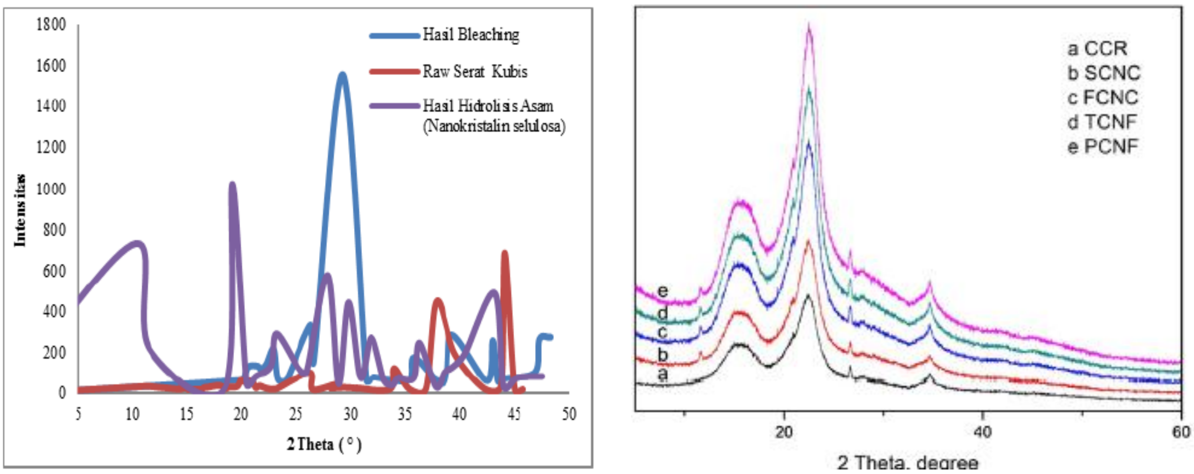
CI_w is the degree of crystallinity using the Wunderlich method

I_c is the area under the crystalline section reflex ;

I_A is the area spectrum of the amorphous region;

K is the proportionality factor, including polarization and Lorenz effect (Thompson–Lorenz factor), temperature correction, and the differences between X-ray densities of amorphous phase.

XRD relates the wavelength of electromagnetic radiation to the diffraction angle and lattice distance in the crystal sample. These diffracted X-rays are then detected, processed and counted. With sufficient sample anglesin the 2Θ angle range, all possible diffraction directions from the lattices must be achieved due to the random orientation of the powder material. The conversion from diffraction peaks to*d-spacing* allows compound identification because each compound has a *unique*set of *d-spacing* . Usually this is achieved by comparing *d-spacing* to astandard reference pattern[65].



(a) (b)

Fig.7. XRD patterns of CNC (a) [67] dan (b) [2]

FT-IR (Fourier Transform Infra-Red)

Infrared spectrophotometer is an instrumentation that uses infrared radiation to determine the functional groups present in organic compounds. The working principle of IR spectrophotometry is the interaction of energy with matter. For instance, in an experiment a molecule of a complex compound is shot with energy from a light source causing the molecule to vibrate. The light source is a ceramics, which when electrified, it can emit infrared. Vibration can occur because the energy from infrared rays are not strong enough to cause atomization of molecule compoundsin a shot where the magnitude of the vibrational energy of each atom is different depending on the atoms and the strength of bonds that be connected to produce different frequencies[16]. Some examples of typical absorption of several functional groups can be seen in

Table10.Typical absorption of several functional groups[16]

Table10.Typical absorption of several functional groups[16].

Compound groups	Absorption area (cm^{-1})
C-H alkane	2850-2960, 1350-1470
C-H alkene	3020-3080, 675-870
C-H aromatic	3000-3100, 675-870
C-H alkyne	3300
C=C alkene	1640-1680
C=C aromatic (polycyclic)	1500-1600
C-O alcohol, carboxylic acid ether, ester	1080-1300
C=O aldehyde, ketone, carboxylic acid, ester	1690-1760
O-H alcohol, phenol (monometer)	3610-3640
O-H alcohol, phenol (ikatan H)	2000-3600 (lebar)
O-H carboxylic acid	3000-3600 (lebar)
N-H amine	3310-3500
C-N amine	1180-1360
$-NO_2$ nitro	1515-1560

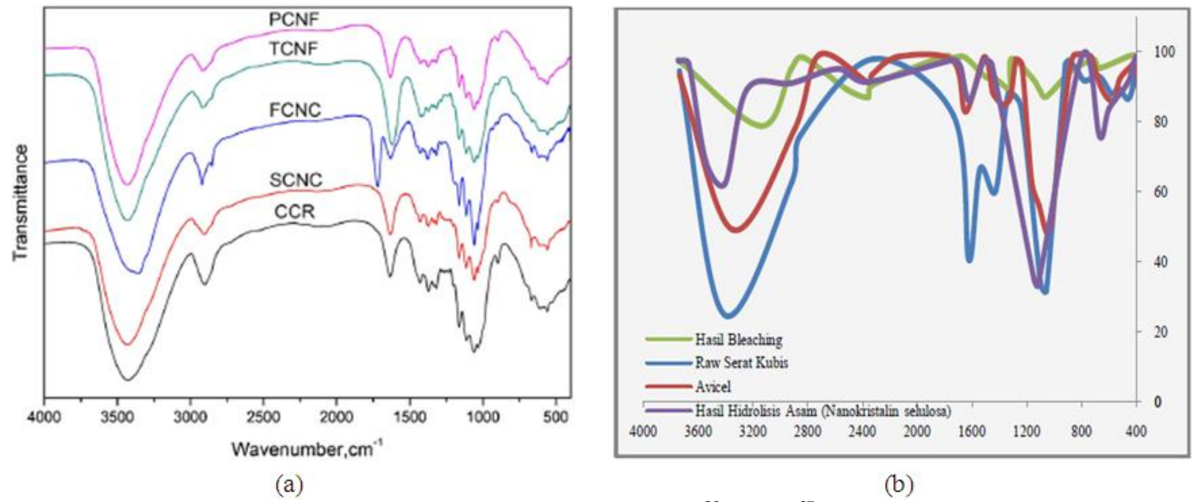


Fig.8.Nanocellulose FT-IR a) [28] dan b) [67]

Surface Morphological Analysis

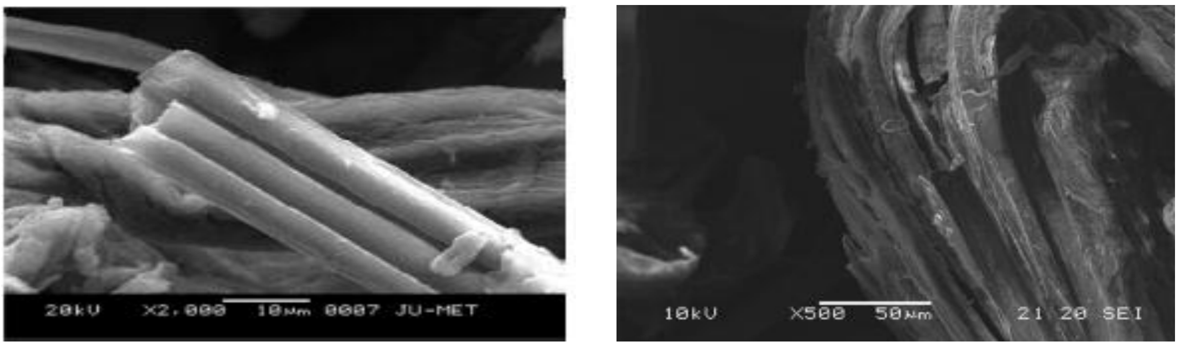
Morphological analysis of the surface is generally using SEM (Scanning Electron Microscopy), AFM (Atomic Force Microscopy) and TEM (Transmission Electron Microscopy). Morphological testing is carried out to see the width, length and distribution. In addition, morphological analysis is used to see other thingssuch as surface modification, mechanics, and optical forms of nanocellulose. Surface morphological analysis also aims to determine the specifications of the nano-crystal Cellulose from various sources, because it is found that the size and shape ofthe nano-crystalline are different based on the source[68].

VII. Preparation of Nanocrystalline Cellulose

Sugarcane Bagasse

From Table1. Isolation of CNC from bagasse.Isolation of CNCfrom bagasse with 5% NaOH and 11%H_2O_2pretreatment for 90 minutes at 55˚C of resulted in 40,35% of α-cellulose[11]. This was greater then CNC production by pretreatment with H_2O_2 15% and NaOH 17,5% for 60 minutesat 80˚C where 20,8% of α-cellulose[21].The results obtained from the manufacture of CNC from bagasse were found to be greater in pretreatment with 15% KOH 2N and15% H_2O_2 at 80˚C for 60 minutes, followed by hydrolysis of 1N HCl acid for 120 minutes at 80˚C. The results obtained were 44.5% of the sample[12].

The highest value of CrI obtained at 83,75%, where the pretreatment by 5% NaOH at 80˚C for180 minutes and H_2O_2 at 80˚C for 1 hour, followed by mechanical treatment under 21,000 rpm[10]. The other CrI values were 42,65% with pretreatment by 3,5% HNO_3 at 90˚C for 120 minutes and 3,5% NaOCl for minutes, and treatment with hydrolyzed acid by 50% H_2SO_4 at 45˚C for 30 minutes[9].



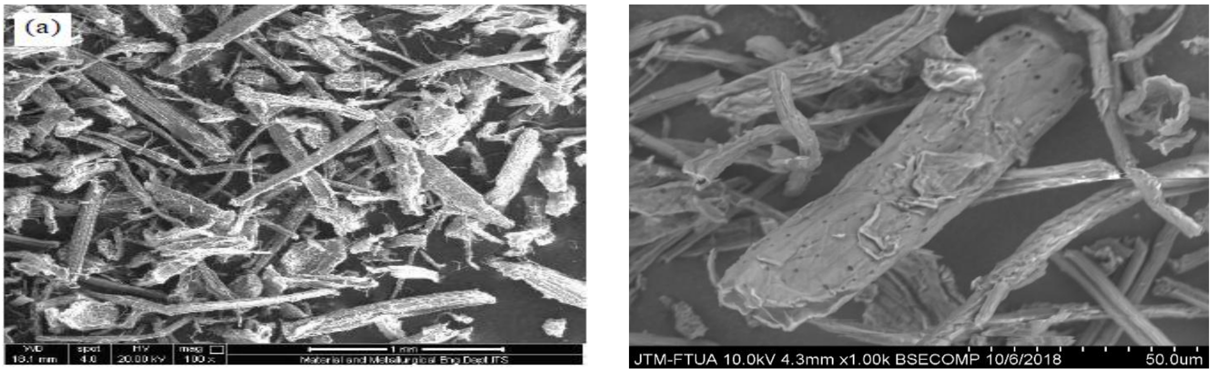
a) b)

Fig.9.SEM of CNCfrom bagasse a) [11] dan b) [64]

Rice Straw

Isolation of crystal cellulose fromrice straw using HCl 2,5 N at 100˚C for 15, 30, 45, and 60 minutes. In this study, it was carried out at the time of pretreatment using various bases for delignificationandbleaching process. There were three treatments, namely using 3,5%HNO_2, 17,5%NaOH, and 13,5% of Sodium perclorate ($NaClO_4$).The results obtained by immersion in 2,5N HCl obtained the highest yields at 60 minutes of immersion, namely 54.54% or 96.72% of the α-celluloseobtained, compared to the immersion time of only 15 minutes, which was 33.83% or 60% of the total α-celluloseobtained[13].While the treatment of rice straw with 20% of NaOH and H_2SO_4pretreatment at 80˚C for 8 hours, then immersed in$H_2SO_4$for 15 minutes at 80˚C, obtained 24% yield,higher than treatment with 2,5 N HCl with the same temperature and immersion time, namely 16.2%[16]see

Table2.



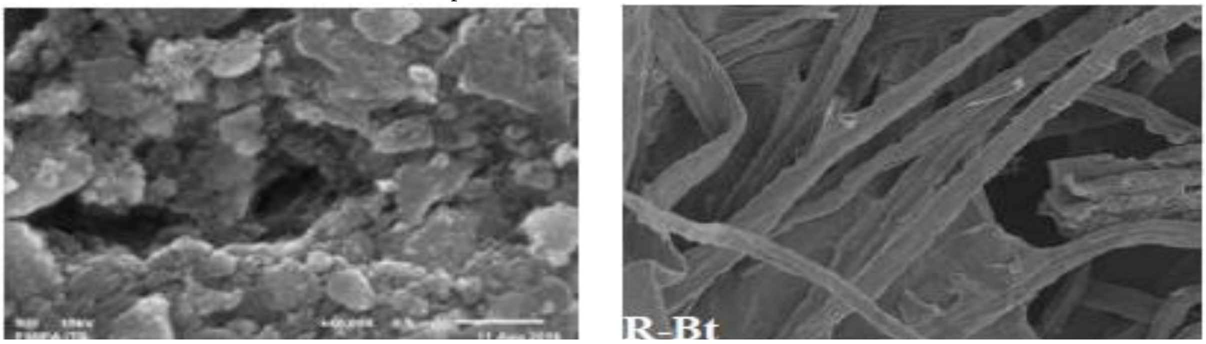
a) b)

Fig.10.SEM of CNC from rice straw a) [15] dan b) [14]

Rice straw processed using 2,5 N HCl at 50˚C for 10 minutes for hydrolysis and 7.5% NaOH for the pretreatment process, obtained a CrI yield of 82%[15].The CrI obtained is almost the same as the hydrolysis of 2,5 N HCl at 100˚C for 15 minutes, which is 78%[14].

Rice Husk

The highest pretreatment result from rice husk samples were obtained by delignification using 4% NaOHand bleaching with 1,7% HCl, with α-cellulose obtained by 96%. The chemical reaction of alkaline NaOH was carried out by reflux method for 120 minutes. Furthermore, bleaching was carried out using 1,7% HCl for 4 hours and refluxed, until the samples obtained turned white[18].



a) b)

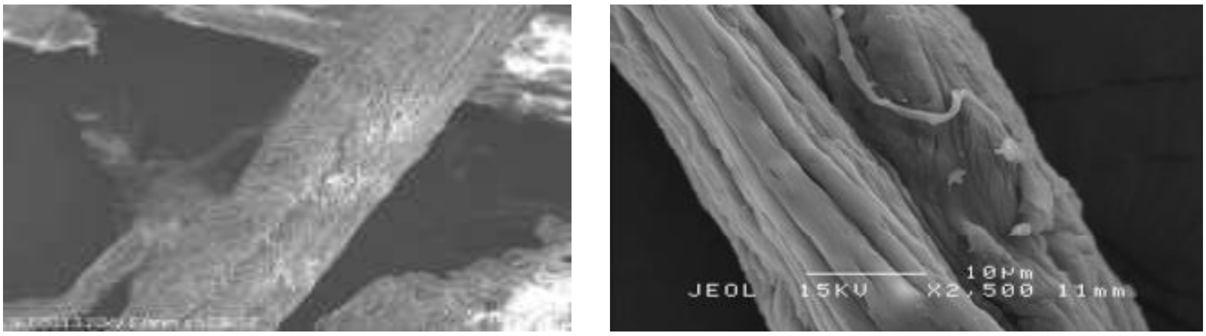
Fig.11.SEM of CNC from rice husk a)[19] dan b) [20]

Treatment of rice husks using hydrolysis of 2,5 N of HCl at 90˚C for 15 minutes then blanched using H2O2 3% 90˚C for 1 hour while stirring, showed the yield obtained was 13,45%. In this study, from 25 g of the sample obtained 3,35 g of cellulose[19].see

Table3.The highest CrI was obtained from 1,7% of HCl and 4% of NaOH pretreatment, and treatment with 10 mol/L H2SO4 was 59%[18]. The lowest CrI value was 50%, obtained from 4% of NaOH and 6,8% of NaCl pretreatment and following by 64% H2SO4 at 50˚C for 40 minutes[20].

Oil Palm Empty Bunches(TKKS)

The highest CNC preparation was obtained by pretreatment with 10% NaOH at 150˚C for 30 minutes. Then, it was blended with 1% NaClO at 80˚C for 1 hour (done three times). The α-celluloseobtained from the sample was 81,11%. Samples obtained from pretreatment were hydrolyzed H_2SO_4 97% with a ratio of 1:80 to samples and solution. The solution was then heated at 50˚C while stirring for 3,5 hours. Furthermore, the sample solution was centrifugeat 10,000 rpm for 15 minutes. After that, the solution was neutralized with distilled water and allowedto stand, then filtered with filter paper. The XRD analysis results showed a 96% crystallinity index[23].



a) b)

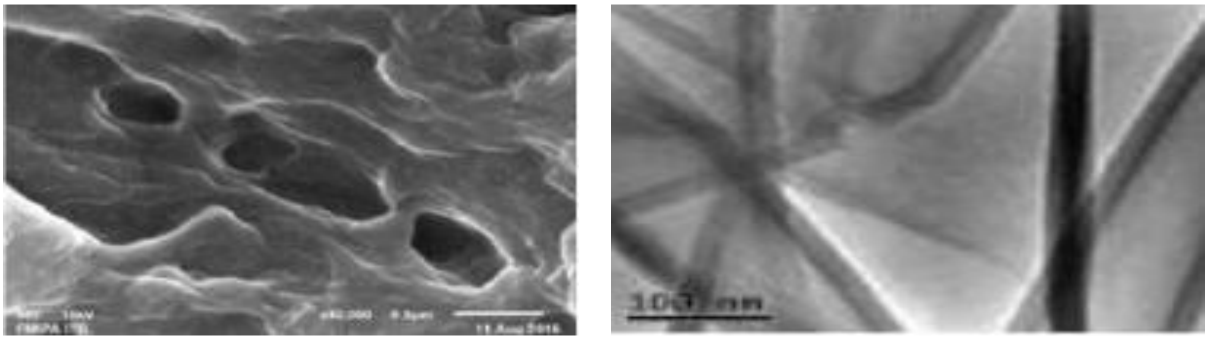
Fig.12.SEM of CNC from oil palm empty bunches a)[21] dan b)[24]

In several studies carried out more systematically, pretreatment for delignification was carried out using HNO_3 3,5% and $NaNO_2$. This aims to dissolve lignin in the form of nitrogen. Furthermore, the process of hemicellulose removalby *swelling* method using 2% NaOH and Na_2SO_3 2%. This process removes hemicellulose,mineral salts, and ash by inflating the sample fibers. After that, to bleach the sample, using 17.5% NaOCl, in addition, 17.5% NaOCl was able to separate α-cellulose from β , and γ- cellulose[25].

Sawdust

The treatment of wood powder usinghydrolysis of 2.5N HCl at 90˚C in 15 minutes and then blended usingH_2O_2 3% at 90˚C for 1 hour whilestirringshowedthe yield obtained was 22.75%. In this study, 25 g of the sample,5,69 g of cellulose were obtained. The wood powder treatment usinghydrolysis of 2.5N HCl at 90˚C in 15 minutes and then blended using H_2O_2 3% at 90˚C for 1 hour whilestirringshowedthe yield obtained was 22,75%. In this study, 25 g of the sample, obtained 5,69 g of cellulose[19].

The highest CrIwas obtainedintreatmentusing H_2SO_4 60% by sonication, under 60% for 60 minutes. The CrI obtained was 90%. After hydrolysis, the sample liquid is mixed with cold aquadest to stop the hydrolysis reaction. The samples were then centrifuged at 12,000 rpm for 10 minutes. Centrifuge is carried out by separating the aggregate withthe solute, in this case to separate crystals and amorphous cellulose. Furthermore, the aggregate contained in this liquid isre-sonicated. The NCC obtained was then frozen-dried (-60 C, 0.1 mbar, a pressure that did not damage the cellulose structure) to obtain the powder[38].

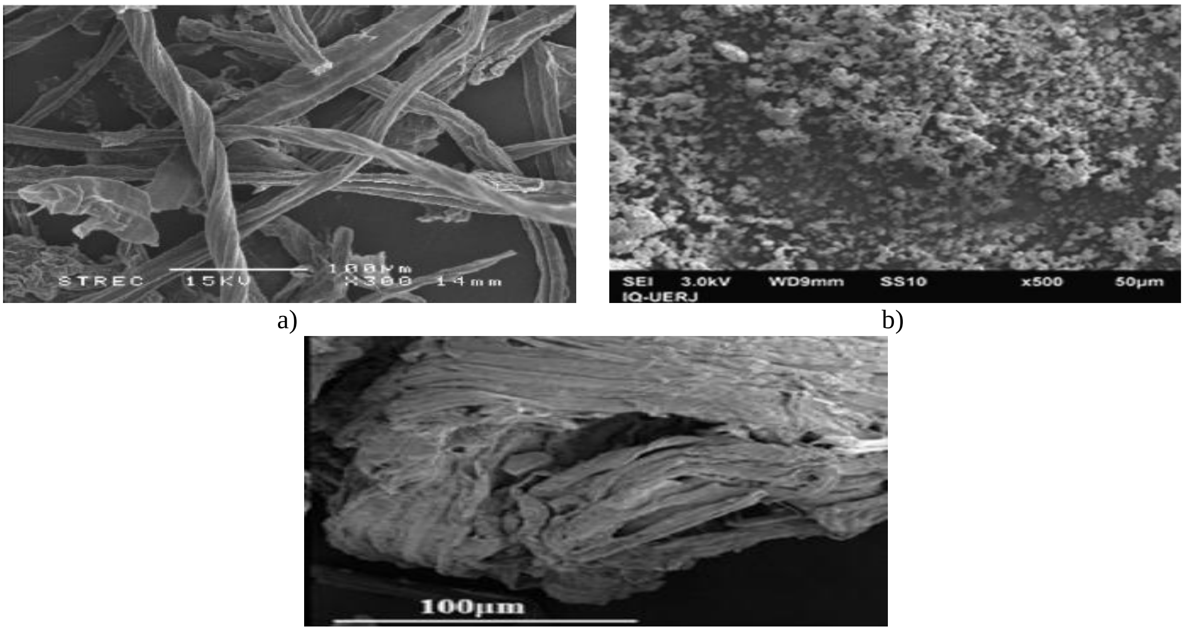


a) b)

Fig.13.SEM of CNCfrom sawdust a)[19]and b)[37]

Corn Waste

Based on several studies on various sources of cellulose in several parts of the corn plant, the highest yield was found in the remaining corn stover, which was 62.1%. These results were obtained by pretreatment of 2% NaOH at 80˚C for 240 minutes and a bleaching process of 1,7% $NaClO_2$ at 80˚C for 360 minutes. Furthermore, the treatment was carried out using 55% H_2SO_4 for 15 minutes at a temperature of 50˚C. The hydrolysis product were then washed with water, then centrifuged three times and washed again with water until pH~6[36].



a) b)

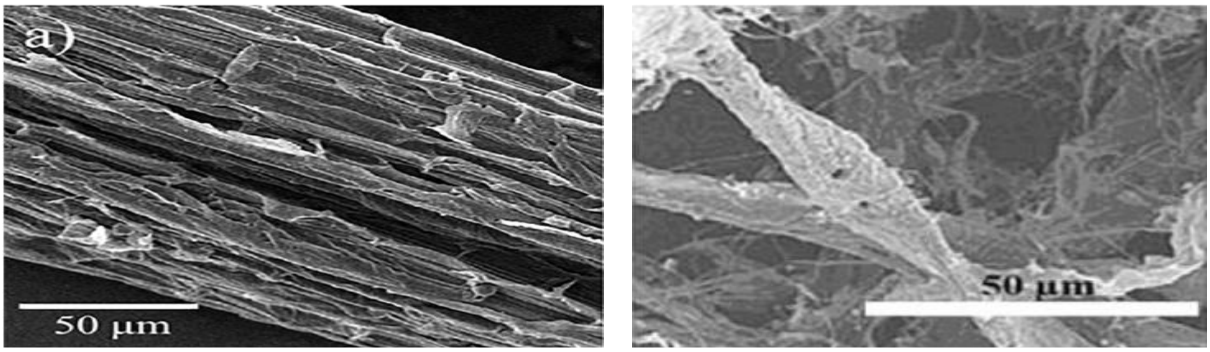
c)

Fig.14.SEM of CNC fromcorn waste a) corn cob [27], b) corn husk [29], dan c) corn stover [35].

The highest CrI was obtained in the hydrolysis reaction of corn husk using 60% H_2SO_4at a temperatureof 40˚C for 300 minutes. Based on these studies, it was found that the CrI can bepredicted by an equation between reactiontime and concentration ofH_2SO_4/sample. Wherethe longer the hydrolysis reaction time, the higher the CrIvalue. It was also found that the hydrolysis reaction began to stabilize at the reaction time above 80 minutes with a large H_2SO_4/sample content of ~25 mL[29].

Pineapple

The highest yield for CNC from pineapple leaves was obtained from pretreatment using 2% NaOH under 138 kPa pressure autoclave for 1 hour, followed by bleaching a mixture of 27% NaOH + CH_3COOH 78,8%+NaClO 1:3in solution, yielding 76% α-cellulose. After that, it was reacted with 11%$H_2C_2O_4$ under 138 kPa pressure in autoclave for 15 minutes. The results of the autoclave were reacted with $KMnO_4$ to remove the acid. The yield of all these reactions gave a yield of 69%[41].



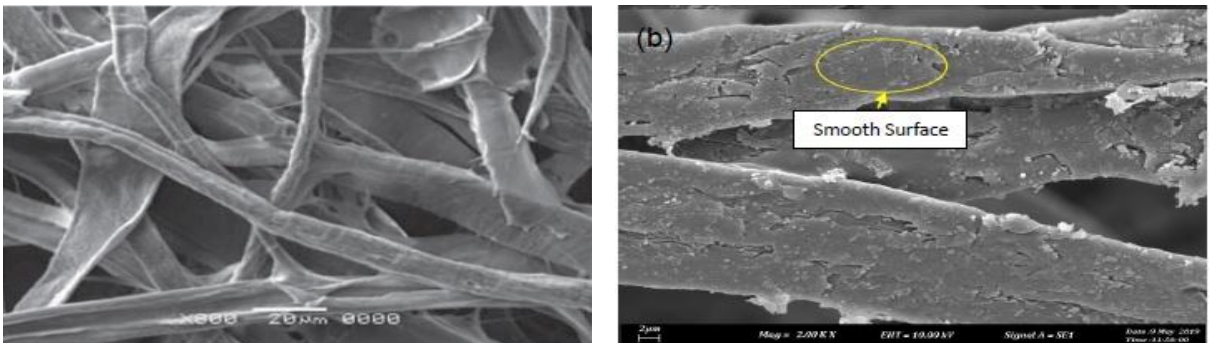
a) b)

Fig.15.SEM of CNC from pineapple a) [42] dan b) [41]

The highest CrI was 92.13%. Itwas obtained by hydrolysiswith 50%H_2SO_4at 50˚C for 60 minutes. After hydrolysis the sample was washed with water by centifugation to remove the acid. Then sonicated 20 Hz for 3 minutes[40].

Paper

The highest α-cellulose production was obtained by pretreatment using 5% NaOH and 2% $NaClO_2$. The amount of α-cellulose obtained increased from 79.58% to 98.7% without and using 2% of $NaClO_2$. The first pretreatment process used 5% NaOH at 125˚C for 2 hours under constant shaking. After that the samples were washed to a neutral pH. The sample was then blended using 2% NaClO2 for 2 hours at a temperature of 125˚C, this treatment was repeated until the white sample was obtained[47].

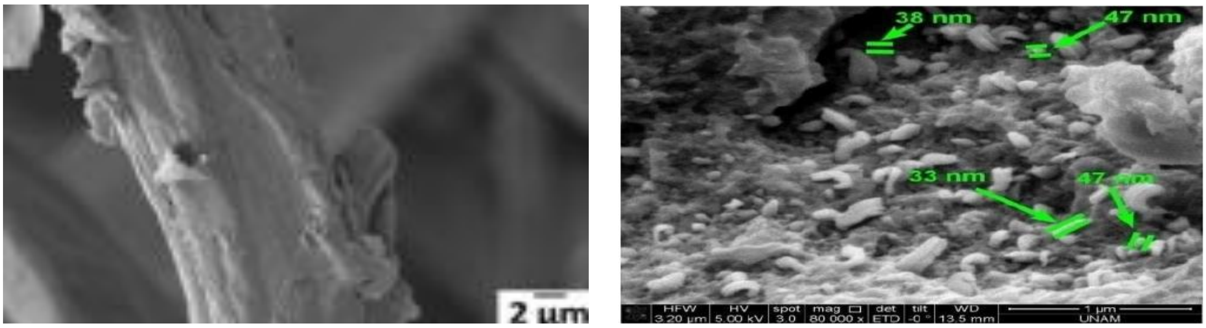


a) b)

Fig.16.SEM of CNCfrom paper a)[49] dan b)[43]

Cotton

One of the optimization studies for Isolation of CNC from cottonfound that the highest yield that could be achieved was 72%. This experiment was carried out in various variations of acid concentration, reaction time, and homogenization rate. From this study, it was found that the best conditions to produce the highest yield among the various acid concentrations (55, 60 and 65%) were 60%, the time (3, 5and7 minutes) were 5 minutes, and the homogenization speed (9000, 10500, and 12000 rpm) was 9000 rpm[51].



a) b)

Fig27. SEM NCC dari Cotton a)[53] dan b)[54]

VIII. Conclusions

The isolation of CNC by strong acid hydrolysis widely uses 64% H2SO4 and 2,5 N HCl. In the isolation of CNC, chemical and mechanical pretreatment are very influential to increase the purity of the α-cellulose produced. Based on several previous studies, the isolation of CNC from various sources found in nature has great potential as a polymer. This provides solutions for human life to expand the scope of recycling organic waste into value-added materials. Further research is needed to see the optimal process of CNC cellulose isolation from various types of specific samples for a wide range of production process.

CNC can be used in a various fields, including water treatment, absorbent, cosmetic products, coatings, fillers, adhesives, nanocomposites, energy and electronics, biomedicine, additive coumpound of drugs, and including of the manufacture of other biomaterials. The advantages of using strong acids in CNC isolation treatment are that they are easy to do, a short process, low cost, and the resulting CNC propertiescan be adjusted based on side group modifications. Meanwhile, the weakness of thestrong acid hydrolysis process is ineffective storage and safety. So, it is not recommended for small scalecommercial industries. However, strong acids are very dangerous for nature because they are toxic and can distrupt the ballance of the ecosystem in water, soil, and air. Further research needs to be done regarding the CNC isolation process that is environmentally friendly, safe, and time and cost efficient.

References

[1]. Lin N, Dufresne A. Nanocellulose in biomedicine: Current status and future prospect. Eur Polym J. 2014;59:302–25.
[2]. Liu C, Li B, Du H, Lv D, Zhang Y, Yu G, et al. Properties of nanocellulose isolated from corncob residue using sulfuric acid , formic acid , oxidative and mechanical methods. Carbohydr Polym. 2016;151:716–24.
[3]. Börjesson M, Westman G. Crystalline Nanocellulose — Preparation , Modification , and Properties. Cellul - Fundam Asp Curr Trends. 2017;
[4]. Habibi Y, Lucia LA, Rojas OJ. Cellulose Nanocrystals : Chemistry , Self-Assembly , and Applications. 2010;110:3479–500.
[5]. Phanthong P, Reubroycharoen P, Hao X, Xu G, Abudula A. Nanocellulose : Extraction and application. Carbon Resour Convers.

2018;
[6]. Sukara E, Meliawati R. Potential Values of BacteriaL Cellulose for industrial applications. J Selulosa. 2015;4(1):7–16.
[7]. Thomas B, Raj MC, Athira KB, Rubiyah MH, Joy J, Moores A, et al. Nanocellulose , a Versatile Green Platform : From Biosources to Materials and Their Applications. Chem Rev. 2017;
[8]. Ioelovich M. Optimal Conditions for Isolation of Nanocrystalline Cellulose Particles. Nanosci Nanotechnol. 2012;2(2):9–13.
[9]. Nisak A. Optimasi Konsentrasi Nanokristalin Selulosa Dari Ampas Tebu (Sugarcane Officinarum) Sebagai Bahan Alternatif Pembuatan Kapsul Bebas Gelatin. Universitas Islam Negeri Maulana Malik Ibrahim Malang; 2018.
[10]. Saputri LH, Sukmawan R, Rochardjo HSB, Rochmadi. Isolasi Nano Selulosa dari Ampas Tebu dengan Proses Blending pada Berbagai Variasi Konsentrasi. In: Seminar Nasional Teknik Kimia "Kejuangan" Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia. Yogyakarta: UPN Veteran Yogyakarta; 2018. hal. 1–6.
[11]. Saha S, Ghosh R. Cellulose Nanocrystals from lignocellulosic agro-waste : A comparative study on Conventional and Ultrasonic Assisted Preparation Methods. In: Materials Today: Proceedings. Elsevier Ltd; 2019. hal. 628–36.
[12]. Azizah Y, Marziah A. Hidrolisis Ampas Tebu (Baggase) menggunakan HCl menjadi Cellulosa Powder. J Ramah Lingkung. 2018;1(2):21–5.
[13]. Rivai H, Djamaan A. Optimization of production and characterization of homolog vivacel from rice straw Optimization of production and characterization of homolog vivacel from rice straw. Der Pharm Lett. 2016;8(19):388–94.
[14]. Rivai H, Ramdani, Andayani R, Armin F, Djamaan A. Preparation And Characterization Of Microcrystalline Cellulose From Rice Straw Using Chemical And Enzymatic Techniques. Int Res J Pharm. 2019;10(7).
[15]. Prasetia, A. IGNJ, Putra IGNAD, Arsana DAMIPS, Prabayanti NPM. Studi Karakteristik Farmasetis Mikrokristalin Selulosa dari Jerami Padi Varietas Lokal Bali. J Sains Mater Indones. 2016;17(3):119–23.
[16]. Okditanisa R. Pembuatan Selulosa Mikrokristal dari Limbah Jerami Padi dan Pemanfaatannya dalam Pembuatan Tablet Glibenklamid Lepas Lambat (Sustained Release). Universitas Andalas; 2019.
[17]. Yunus MA, Raya I, Tuara ZI. Synthesis cellulose from rice husk. Indones Chim Acta. 2019;12(2):79–83.
[18]. Johar N, Ahmad I, Dufresne A. Extraction , preparation and characterization of cellulose fibres and nanocrystals from rice husk. Ind Crops Prod. 2012;37(1):93–9.
[19]. Andalia R, Helwati H. Isolation and characterization of cellulose from rice husk waste and sawdust with chemical method. J Nat. 2020;20(1):6–9.
[20]. Collazo-bigliardi S, Ortega-toro R, Boix AC. Isolation and characterisation of microcrystalline cellulose and cellulose nanocrystals from coffee husk and comparative study with rice husk. Carbohydr Polym. 2018;191:205–15.
[21]. Maria WE, Kusumawati E, Regiana A, Suminar DR. Production Nanocellulose from Raw Materials For Oil Palm Empty Bunches (TKKS) with Hydrolysis and Freeze Drying Methods. IOP Conf Ser Mater Sci Eng. 2020;742(012033).
[22]. Julianto H, Farid M, Teknik D, Industri FT, Teknologi I, Nopember S. Ekstraksi Nanoselulosa dengan Metode Hidrolisis Asam sebagai Penguat Komposit Absorpsi Suara. 2017;6(2):242–5.
[23]. Burhani D, Septevani AA. Isolation of Nanocellulose from Oil Palm Empty Fruit Bunches Using Strong Acid Hydrolysis. In: Proceedings of the 4th International Symposium on Applied Chemistry 2018. American Institute of Physics; 2018.
[24]. Chieng BW, Lee SH, Ibrahim NA, Then YY, Loo YY. Isolation and Characterization of Cellulose Nanocrystals from Oil Palm Mesocarp Fiber. Polymers (Basel). 2017;9(355):1–11.
[25]. Putri E, Gea S. Isolasi Dan Karakterisasi Nanokistral Selulosa Dari Tandan Sawit (Elaeis Guineensis Jack). Elkawnie J Islam Sci Technol. 2018;4(1):13–22.
[26]. Singh HK, Patil T, Vineeth SK, Das S, Pramanik A, Mhaske ST. Isolation of microcrystalline cellulose from corn stover with emphasis on its constituents : Corn cover and corn cob. Mater Today Proc. 2019;
[27]. Kampeerapappun P. Extraction and Characterization of Cellulose Nanocrystals Produced by Acid Hydrolysis from Corn Husk. J Met Mater Miner. 2015;25(1):19–26.
[28]. Du C, Li H, Li B, Liu M, Zhan H. Characteristics and Properties of Cellulose Nanofibers Prepared by TEMPO Oxidation of Corn Husk. BioResources. 2016;11(2):5276–84.
[29]. Mendes CA de C, Ferreira NMS, Furtado CRG, Sousa AMF de. Isolation and characterization of nanocrystalline cellulose from corn husk. Mater Lett. 2015;148:26–9.
[30]. Smyth M, García A, Rader C, Foster EJ, Bras J. Extraction and process analysis of high aspect ratio cellulose nanocrystals from corn (Zea mays) agricultural residue. Ind Crop Prod. 2017;108:257–66.
[31]. Yang X, Han F, Xu C, Jiang S, Huang L, Liu L. Effects of preparation methods on the morphology and properties of nanocellulose (NC) extracted from corn husk. Ind Crop Prod. 2017;109:241–7.
[32]. Harahap H, Nasution AH, Junaidi IF. Pengaruh Konsentrasi Asam Sulfat (H2SO4) pada Hidrolisa Tongkol Jagung (Zea mays) Menjadi Nanokristal Selulosa sebagai Filler Penguat pada Produk Lateks Karet Alam. J Tek Kim USU. 2019;08(2):48–53.
[33]. Hernandez CC, Ferreira FF, Rosa DS. X-ray powder diffraction and other analyses of cellulose nanocrystals obtained from corn straw by chemical treatments. Carbohydr Polym. 2018;193:39–44.
[34]. Liu Z, He M, Ma G, Yang G, Chen J. Preparation and Characterization of Cellulose Nanocrystals from Wheat Straw and Corn Stalk Preparation and Characterization of Cellulose Nanocrystals from Wheat Straw and Corn Stalk. J Korea TAPPI. 2019;51(2):40–8.
[35]. Huang S, Zhou L, Li M-C, Wu Q, Zhou D. Cellulose Nanocrystals (CNCs) from Corn Stalk : Activation Energy Analysis. Materials (Basel). 2017;1–13.
[36]. Costa LADS, Fonsêca AF, Pereira F V., Druzian JI. Extraction And Characterization Of Cellulose Nanocrystals From Corn Stover. Cellul Chem Technol. 2015;49(2):127–33.
[37]. Ferreira RR, Souza AG, Nunes LL, Rangari VK, Rosa S. Use of ball mill to prepare nanocellulose from eucalyptus biomass: challenges and process optimization by combined method. Mater Today Commun. 2020;22(100755).
[38]. Shaheen TI, Emam HE. Sono-chemical synthesis of cellulose nanocrystals from wood sawdust using Acid hydrolysis. Int J Biol Macromol. 2017;107:1599–606.
[39]. Marcos R, Pires W, Neto F, Alves H, Ferreira D, Oliveira N, et al. Cellulose nanocrystals from pineapple leaf , a new approach for the reuse of this agro-waste. Ind Crop Prod. 2013;50:707–14.
[40]. Pereira PHF, Ju´nior HLO, Coutinho LV, Duchemin B, Cioff MOH. Obtaining cellulose nanocrystals from pineapple crown fibers by free-chlorite hydrolysis with sulfuric acid : physical , chemical and structural characterization. Cellulose. 2020;6.
[41]. Cherian BM, Leão AL, Souza SF de, Costa LMM, Olyveira GM de, Kottaisamy M, et al. Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications. Carbohydr Polym. 2011;86(4):1790–8.
[42]. Prado KS, Spinacé MAS. Isolation and characterization of cellulose nanocrystals from pineapple crown waste and their potential uses. Int J Biol Macromol. 2018;122:410–6.
[43]. Awang NNA, Munawar RF, Abidin MZZ, Manaf MEA, Mohamad N, Ahmad SSS. Extraction and Characterisation of Cellulose

Nanocrystals Structures from Waste Office Paper. J Adv Res Fluid Mech Therm Sci. 2019;2(2):202–11.
[44]. Das K, Ray D. Study of the Properties of Microcrystalline Cellulose Particles from Different Renewable Resources by XRD , FTIR , Nanoindentation , TGA and SEM. J Polym Env. 2010;18:355–63.
[45]. Zaki ASC, Yusoff NA, Rohaizad NM, Sohaimi KSA, Mohamed AR, Salleh NHM, et al. Isolation and Characterization of Nanocellulose Structure from Waste Newspaper. J Adv Res Eng Knowl. 2018;5(1):27–34.
[46]. Campano C, Miranda R, Merayo N, Negro C, Blanco A. Direct production of Cellulose Nanocrystals from old newspapers and recycled newsprints. Carbohydr Polym. 2017;
[47]. Mohamed MA, Salleh WNW, Jaafar J, Asri SEAM, Ismail AF. Physicochemical properties of "green" nanocrystalline cellulose isolated from recycled newspaper. RSC Adv. 2015;5:29842–9.
[48]. Souza AG De, Rocha DB, Kano FS, Rosa S. Valorization of industrial paper waste by isolating cellulose nanostructures with different pretreatment methods. Resour Conserv Recycl. 2019;143:133–42.
[49]. Van-Pham D-T, Pham TYN, Tran MC, Nguyen C-N, Tran-Cong-Miyata Q. Extraction of thermally stable cellulose nanocrystals in short processing time from waste newspaper by conventional acid hydrolysis. Mater Res Express. 2020;7(065004).
[50]. Haleem N, Arshad M, Shahid M, Tahir MA. Synthesis of carboxymethyl cellulose from waste of cotton ginning industry. Carbohydr Polym. 2014;113:249–55.
[51]. Hemmati F, Jafari SM, Taheri RA. Optimization of homogenization-sonication technique for the production of cellulose nanocrystals from cotton linter. Int J Biol Macromol. 2019;137:374–81.
[52]. Jordan JH, Condon BD, Easson MW, Dien B, Thompson S. Extraction and characterization of nanocellulose crystals from cotton gin motes and cotton gin waste. Cellulose. 2019;26(10):5959–79.
[53]. Maciel MMÁD, Benini KCC de C, Voorwald HJC, Cioff MOH. Obtainment and characterization of nanocellulose from an unwoven industrial textile cotton waste : Effect of acid hydrolysis conditions. Int J Biol Macromol. 2019;126:496–506.
[54]. Al-khateeb IKI, Hussin SM, Al-obaidi YM. Extraction of Cellulose Nano Crystalline from Cotton by Ultrasonic and Its Morphological and Structural Characterization. Int J Mater Chem Phys. 2019;1(2):99–109.
[55]. Thambiraj S, Shankaran DR. Preparation and physicochemical characterization of cellulose nanocrystals from industrial waste cotton. Appl Surf Sci. 2017;412:405–16.
[56]. Zhang H, Chen Y, Wang S, Ma L, Yu Y, Dai H, et al. Extraction and comparison of cellulose nanocrystals from lemon (Citrus limon) seeds using sulfuric acid hydrolysis and oxidation methods. Carbohydr Polym. 2020;238(116180).
[57]. Sofla MRK, Brown RJ, Tsuzuki T, Rainey TJ. A comparison of cellulose nanocrystals and cellulose nano fibres extracted from bagasse using acid and ball milling methods. Adv Nat Sci Nanosci Nanotechnol. 2016;7(035004).
[58]. Granström M. Cellulose Derivatives : Synthesis , Properties and Applications. University of Helsinki Finland; 2009.
[59]. Nuringtyas TR. Karbohidrat. Univ Gajah Mada. 2010;
[60]. Badshah M, Ullah H, Ali S, Joong K, Park K. Preparation , characterization and in-vitro evaluation of bacterial cellulose matrices for oral drug delivery. Cellulose. 2017;24(11):5041–52.
[61]. Bhat AH, Dasan YK, Khan I, Soleimani H, Usmani A. Application of nanocrystalline cellulose: Processing and biomedical applications. In: Jawaid M, Boufi S, H.P.S. AK, editor. Cellulose-Reinforced Nanofibre Composites. Woodhead P. Elsevier Ltd; 2017. hal. 215–40.
[62]. Mandal A, Chakrabarty D. Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. Carbohydr Polym. 2011;86(3):1291–9.
[63]. Lubis S, Karsono, Nasution MP, Gea S. Preparation and Characterization of Nanocrystalline Cellulose from Sugar Palm Bunch (Arenga pinnata (Wurmb) Merr .). Int J PharmTech Res. 2014;6(2):814–20.
[64]. Lam NT, Chollakup R, Smitthipong W, Nimchua T, Sukyai P. Characterization of Cellulose Nanocrystals Extracted from Sugarcane Bagasse for Potential Biomedical Materials. Sugar Tech. 2017;19(5):539–52.
[65]. Bunaciu AA, Udristioiu EG, Aboul-Enein H. X-Ray Diffraction Instrumentation And Application. Crit Rev Anal Chem. 2015;45(4):289–99.
[66]. Szymariska-Chargot M, Chyliriska M, Gdula K, Koziol A, Zdunek A. Isolation and Characterization of Cellulose from Different Fruit and Vegetable Pomaces. Polymers (Basel). 2017;9(495).
[67]. Arjuna A, Natsir S, Khumaerah AA, Yulianty R. Modifikasi serat limbah kubis menjadi nanokristalin selulosa melalui metode hidrolisis asam. Galen J Pharm. 2018;4(2):119–25.
[68]. Alle M, Bandi R, Lee S, Kim J. Recent trends in isolation of cellulose nanocrystals and nanofibrils from various forest wood and nonwood products and their application. In: Husen A, Jawaid M, editor. Nanomaterials for Agriculture and Forestry Applications. Elsevier; 2020. hal. 41–80.