Synthesis and Characterization of Nanonitrocellulose from Water Hyacinth for Application of Solid Propellant Formulations

Ashagrie Zewudu Ayelgn

A Thesis Submitted to

Department of Chemical Engineering

School of Mechanical, Chemical, and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

June, 2024

Adama, Ethiopia

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Co-Advisor: Dr. Wondalem Misganaw

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DECLARATION

I hereby declare that this Master Thesis entitled "**Synthesis and Characterization of Nanonitrocellulose from Water Hyacinth for Application of Solid Propellant Formulations**" is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Ashagrie Zewudu Ayelgn	_____	_____
Name the student	Signature	Date

RECOMMENDATION

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled "**Synthesis and Characterization of Nanonitrocellulose from Water Hyacinth for Application of Solid Propellant Formulations**" prepared under our guidance by Ashagrie Zewudu Ayelgn submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical Engineering. Therefore, we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

Dr. Zelalem Tumsa		
Major advisor	Signature	Date
Dr. Wondalem Misganaw		26 June 2024
Co–advisor	Signature	Date

APPROVAL PAGE

We, the advisors of the thesis entitled "**Synthesis and Characterization of Nanonitrocellulose from Water Hyacinth for Application of Solid Propellant Formulations**'' and developed by Ashagrie Zewudu Ayelgn, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Dr. Zelalem Tumsa		
Major advisor	Signature	Date
Dr. Wondalem Misganaw		26 June 2024
Co–advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Ashagrie Zewudu Ayelgn have read and evaluated the thesis entitled "**Synthesis and Characterization of Nanonitrocellulose from Water Hyacinth for Application of Solid Propellant Formulations**'' and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering.

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Finally, approval and acceptance of the thesis is contingent upon submission of its final Copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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LIST OF ABBREVIATIONS

AP-NC	Ammonium perchlorate nitrocellulose
ASTM	American standard testing method
ASTU	Adama Science and Technology University
ATR	Attenuated total reflectance
BC	Bacterial cellulose
CNF	Cellulose nanofiber
CRP	Carbon reactive protein
DSC	Diffraction scanning calorimetry
DMF	Dimethylformamide
DS	Degree of substitution
ES	Electrospinning
FC	Fixed carbon
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width half maximum
MCC	Micro crystalline cellulose
MCLW	Metal clad leaky waveguide
NBC	Bacterial cellulose nitrate
NC	Nitrocellulose
NCC	Nano crystalline cellulose
NCNC	Nanocrystalline nitrocellulose
NCNF	Nitrocellulose nanofiber

OH	Hydroxide
PDI	polydispersity index
PSA	Particle size analyzer
SEM	Scanning electron microscopy
TAPPI	Technical Association of Pulp and Paper Industry
TGA	Thermos gravimetric analysis
VM	Volatile matter
WHC	Water hyacinth-based cellulose
WH	Water Hyacinth
XRD	X-ray diffraction
Cal	calorie
g	gram

Abstracts

Nitrocellulose has attracted the interest of researchers due to its numerous applications, including gun propellant and other industries such as paints, medicines, adhesives, and celluloids. The aim of this study is to synthesize and characterize nanonitrocellulose from water hyacinth to be used in solid propellant formulations. The novelty was in exploring the possibility of synthesizing nanonitrocellulose with a high percentage of nitrogen content from water hyacinth feedstock for the first time. The experiments were carried out after nanocellulose was extracted from water hyacinth using chemical and mechanical treatments including sample preparation, Soxhlet extraction, alkaline treatment, bleaching, sulfuric acid hydrolysis, ultrasonic homogenization, and lyophilization followed by nitration with subsequent stabilization steps by using one factor at a time experimental design at nitrating acid mixture to cellulose ratio (20:1-40:1) ml/g, sulfuric to nitric acid ratio (2.4–3.6), nitrating time (20-60) min, and nitration temperature (20-40) ℃. The extracted nanocellulose was characterized using PSA, XRD, FTIR, SEM, and TGA-DSC to determine the size, crystallinity, functional groups, morphological changes, and thermal stability, respectively. The nitrated nanocellulose (DS = 2.58) was also characterized by elemental analysis, bomb calorimetry, TGA-DSC, FTIR, and SEM to determine the nitrogen content, calorific value, thermal stability and decomposition properties, functional group, and morphological changes, respectively. Experimental findings confirmed the successful synthesis of the desired pure and thermally stable nanosized cellulose (91.3 nm) with a higher crystallinity index (76%) compared to bleached cellulose (54%), and energetic nanonitrocellulose having a high degree of substitution (DS) of 2.58, a calorific value of 10.04 KJ/g, and a density of 1.842 g/cm^3. FTIR also detected the basic hydroxide and nitro functional groups present in nanocellulose and nanonitrocellulose, respectively. In addition, thermogravimetric analysis and differential scanning calorimetry showed the resultant NCNC to have good thermal property and high purity, with a thermal degradation onset temperature of 208.9 ℃ and a heat of decomposition of 9.72 KJ/g, which is sufficient to produce pressure for propellant application. Thus, the nanonitrocellulose obtained from this unconventional feedstock, water hyacinth, is a promising candidate as an ingredient in nitrocellulose-based propellants.

***Keywords**: propellant; water hyacinth; nanocellulose; nitration; nanonitrocellulose; degree of substitution*

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the Study

Nowadays, the demand for renewable and sustainable polymers and their utility as precursors to generate high-energy-dense materials is emerging as an exciting new research environment (Trache et al., 2016). One of the most abundant and renewable biopolymers on this planet, which may be obtained from agricultural waste or biomass, is cellulose, with an annual production of 75.09 tons (Sumiyyah et al., 2016). The presence of a large amount of high-energy hydroxyl functional groups (OH) on the cellulose chain facilitates the chemical functionalization of cellulose and its derivatives with various chemical functional groups such as nitramines, azides, tetrazole, and nitrate esters to form diverse advanced energetic polymers (A. F. Tarchoun et al., 2019). Similarly, the blessings of cellulose-based materials over synthetic polymers are associated with their clean guidance, excessive abundance, renewability, cost effectiveness, and environmental friendliness (Hu et al., 2019).

Among cellulose-primarily based energetic materials, nitrocellulose (NC) remains one of the most popular energetic polymers in gun powders and double-base rocket propellants (Trache, 2017). Due to its noticeable properties, which include terrific mechanical features, top solubility, compatibility with several additives, fast drying rate, flammability, and explosiveness, it has been substantially used in numerous military and civilian applications for many years (Trache, 2019). However, its chemical instability, excessive sensitivity to impact, low density, excessive brittleness, and low combustion temperature have increased the demand for its replacement (Trache et al., 2016). Therefore, physical and chemical modifications of cellulose precursors have been adopted during the last few years to surpass the existing shortcomings associated with the use of traditional cellulose nitrate and to develop new alternative cellulose-based energetic polymers with improved properties. Results mentioned in recent publications confirm that using MCC or NCC as a polymer precursor significantly enhances the properties of the produced energetic polymer (Sumiyyah et al., 2016). In another investigation, Dobrynin and co-workers investigated the use of a novel efficient physical modification of raw nitrocellulose fibers primarily

based on the supercritical antisolvent method to produce nitrocellulose nanoparticles with improved burning rate and decreased sensitivity (Dobrynin et al., 2019). On the other hand, the chemical derivatization of cellulose and its derivative (MCC) has received a great deal of attention from the research community to produce new highly engineering materials from cellulose precursors (Dacrory & Fahim, 2019). In another research study, a novel, promising azides-based cellulose energetic polymer was synthesized by the grafting of glycidyl azides onto the cellulose surface (Krumm et al., 2021). The obtained results revealed the enhanced energy density and insensitivity characteristics of the novel energetic binder compared to traditional cellulose nitrate.

Nitrocellulose, also called cellulose nitrate, is produced commercially because it has desirable demands, together with the manufacturing of ink and lacquers, paper, and cardboard, in addition to formulations for smokeless gun propellant and dynamites (Gismatulina & Budaeva, 2017). Nitrocellulose can be composed of cellulose, which has been obtained from various sources; both natural and synthetic. Plants are the main natural source of cellulose and has been extensively used in industries (X. I. Chen, 2014). But the problem with cellulose-based plants is that they do not exist in pure form, as they contain cellulose with lignin, hemicelluloses, pectin, and starch (Buldum et al., 2017).

Furthermore, some studies have found that lignin and hemicellulose are hard to remove. Any other supply of cellulose, bacterial cellulose (BC), was used as an opportunity to replace plants because of its specific shape and properties. Nata de coco, which incorporates cellulose as a major constituent, was produced with the aid of fermenting coconut water with a subculture of bacteria. At some point in the manufacturing of Nata de Coco, microorganisms metabolize glucose as a carbon source in the coconut water, which is then converted into BC (Bernardo et al., 1998). BC is a hydrophilic polymer with high purity compared to cellulose acquired from different sources. When nitrated, a number of hydroxyl groups from BC are exchanged with nitro groups to form bacterial cellulose nitrate (NBC). NBC with excessive nitrogen content is anticipated to have the capability of being an energetic material. In 1832, nitrocellulose was synthesized by means of the reaction of cotton and wood pulp (a cellulose source) with concentrated nitric acid. But it produced heterogeneous and risky substances with a low nitrogen content of around 4–5% (Torre, 2012). Previous researchers have additionally attempted various methods for synthesizing nitrocellulose from cellulose, together with reacting the aggregate of nitric acid and phosphoric acid, nitric acid

and acetic acid combinations, nitric acid, and organic solvents (Hasnawati et al., 2020). But there have been a few boundaries when using those kinds of methods. As an example, the use of a nitric acid and acetic acid mixture has a tendency to form acetyl nitrate that can explode at an increased temperature (Lopez-Lopez et al., 2011).

The water hyacinth is one of the potential natural fibers containing cellulose, which is considered a weed plant in a water environment with a depleting aquatic ecosystem. WH fiber is a natural fiber material that is not yet widely used because it has various potencies. The chemical content of WH fibers is about 60% cellulose, 8% hemicellulose, and 17% lignin, as reported by (Adekunle, 2010). Consequently, there is potential to transform water hyacinth into a bioresource for possible commercial utility. Relying on the nitrogen content of the material, cellulose nitrate serves numerous functions. Nitrocellulose with an excessive nitrogen content (above 12.5%) is appropriate for propellant; at the same time, nitrocellulose with a low nitrogen content (below 12.5%) may be used for different applications, including printing ink, varnishes, and coatings (Demilitarization & Energetics, 2018).

The novelty of this study is to investigate the use of water hyacinth as a new raw material for the isolation of nanocrystalline cellulose and to intend to undergo nitration to produce nano-nitrocellulose, which is used as an energetic ingredient in gun propellant. Even though natural cellulose is a predominant feedstock in the industrial production of cellulosic nitrate, it is also found in cotton, which is very luxurious and adds excessive value to the final product. Therefore, the objective of this study is to investigate the possibility of converting water hyacinth (Eichhornia crassipes) through chemical treatments into cellulose nitrate. The effects of conditions including nitrating acid mixture to cellulose material ratio, sulfuric acid to nitric acid ratio, nitrating temperature, and nitrating time were investigated. Furthermore, a series of instrumental tools, including elemental analysis, bomb calorimetry, particle size analyzers, FTIR, XRD, SEM, and TGA, were used for the characterization of raw water hyacinth, isolated cellulose, nanocellulose, and nanonitrocellulose.

1.2. Statement of the Problem

Throughout their lifecycle, polymers from petroleum sources are associated with many environmental problems. The development and discovery of biodegradable polymers is of widespread interest to replace polymers from petroleum sources (Medicine & Paulo, 2014). In this

study, nano-nitrocellulose was synthesized from water hyacinth, a fresh plant that has been rapidly grown and spread all over the world. For instance, Lake Tana is the largest highland lake in Ethiopia and it's total shoreline length estimated was 385 km with over 30% is covered with water hyacinth (Bayable et al., 2023). This was a big problem a big challenge due to its ability to quickly cover entire bodies of water and poses serious socio-economic and environmental problems. So, due to its high contents of cellulose, impressive growth rate, and no competition on land use, it is used as a lignocellulosic material source to produce cellulose nitrate. It makes more sense to generate cellulose nitrate from this fast-growing renewable plant with respect to the economic and ecological benefits. Furthermore, the production of advanced energetic materials and propellants is a challenging and active research topic. Developing energetic materials with higher energy release, faster burning rates, controlled ignition, and safer to use is of great interest. Many authors pointed out that the chemical modification of cellulose with nitrogen-rich functional groups such as tetrazole and nitramine can yield valuable energetic polymer alternatives to conventional NC (Krumm et al., 2021). Although there has been previous research on NC synthesis, including that from non-woody raw materials and bacterial cellulose, there is no account of the synthesis of NC from water hyacinth. Propellants, which can be used for military applications, consist of high-energy-density biopolymers up to 60% (Padgett & Drawings, 1974). So, there is potential to synthesize this component in Ethiopia from low-cost water hyacinth to substitute for imported propellants.

1.3. Research Questions

- ✓ Can it be possible to isolate and extract nanocellulose from water hyacinth?
- ✓ Is it possible to synthesize nano-nitrocellulose from water hyacinth (Eichhornia crassipes) with the desired degree of nitration?
- ✓ What are the effects of nitration conditions such as nitrating acid to cellulose ratio, nitration time, and nitration temperature on the yield of nano-nitrocellulose in terms of the degree of nitration?

1.4. General and Specific Objectives

1.4.1. General Objective

The aim of this study is to synthesize and characterize nanonitrocellulose from water hyacinth (Eichhornia crassipes) for solid propellant formulations.

1.4.2. Specific Objectives

- ✓ To characterize the raw water hyacinth (Eichhornia crassipes).
- ✓ To synthesize and characterize cellulose nanocrystals and nano-nitrocellulose.
- ✓ To investigate the effects of sulfuric acid to nitric acid ratio, nitrating acid to cellulose ratio, nitration time, and nitration temperature on the degree of substitution of nanonitrocellulose.
- ✓ To evaluate the energetic performance of synthesized nano-nitrocellulose.

1.5. Significance of the Study

This study is important in that it could provide an opportunity for the conversion of waste water hyacinth as an alternative raw material into valuable nitrocellulose production. Since water hyacinth is a biodegradable raw material, its utilization to produce nitrocellulose helps solve related environmental problems. On the one hand, it is used to remove water hyacinth from water bodies, further reducing waste in landfills. As a result, it helps to keep the aquatic environment and everyday environment safer. Moreover, from an economic point of view, the use of this inexpensive raw material reduces the final production cost of nanonitrocellulose. For the researchers, it opens up a new area of research on bioenergetic polymers for propellant application from waste hyacinth.

1.6. Scope of the Study

This thesis study focuses on fundamental investigations into the use of water hyacinth for the synthesis of nano-nitrocellulose. Firstly, the raw material, water hyacinth, was characterized for its content. Nanocellulose was then synthesized via acid hydrolysis at optimized reaction temperatures, reaction times, and acid concentrations. The resulting nanocellulose was purified using successive centrifugations. The nanocellulose suspension is then sonicated to get a homogenized dispersion, lyophilized, and characterized. Finally, nanocellulose was nitrated with a mixture of sulfuric acid and nitric acid to obtain nano-nitrocellulose, and it was characterized. Further, the effects of process parameters on the yield of nano-nitrocellulose in terms of degree of substitution were investigated, and the energetic performance of the synthesized nano-nitrocellulose was evaluated.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Overview of Lignocellulosic Biomass

Lignocellulosic biomass is one of the most important renewable resource materials worldwide and contains a variety of natural organic matter, mainly associated with plants (Chirayil et al., 2014). It is the largest sustainable carbon-based group and the most promising raw material for the sustainable production of high value-added products (Phanthong et al., 2018). Different regions of the world have many types of useful fiber plants with many uses. The global production of lignocellulosic biomass is estimated at about 1.3×10^{10} metric tons per year (Nguyen et al., 2021). These lignocelluloses are derived from (i) agricultural wastes (palm trunk and empty fruit bunch, corncobs, wheat straw, sugarcane bagasse, coconut husks, wheat rice, and empty fruit bunches); (ii) forest residues (hardwood and softwood); (iii) energy crops (switchgrass); (iv) food wastes; and (v) municipal and industrial wastes (waste paper and demolition wood) (Phanthong et al., 2018). Transitioning these cheap and abundantly available lignocellulosic materials into products with superior functionality is a viable option for improving energy security and reducing greenhouse gas emissions.

It can be considered a major source for the production of biofuel, biochemicals, biopolymer materials, and other value-added products for economic and sustainable development (Soetaredjo et al., 2016). Lignocellulosic fibers are excellent raw materials for the chemistry of polymers and composites, as evidenced by numerous patents and national and international publications, in addition to numerous products already on the market (De Sá et al., 2015). Materials derived from renewable biological sources have the potential to replace petroleum-based synthetic products because they are relatively low-cost, environmentally friendly, readily available, renewable, and nontoxic (Mondal, 2017). Among these materials, cellulosic nanomaterials derived from renewable lignocellulosic biomass may play an important role in the field of nanotechnology research (Fortunati et al., 2016). In this concept, the production of novel, low-cost, and high-performance cellulosic nanomaterials (nanocellulose) from renewable and sustainable resources is a growing research area, as they offer unique physicochemical properties and have received

increasing attention in the last decade (C. Liu et al., 2016; Fortunati et al., 2016). In recent years, the extraction and utilization of nanocellulose from many agricultural and industrial wastes have attracted attention. The cell wall structure of lignocellulosic biomass is mainly composed of components such as cellulose, hemicellulose, lignin, and some extraneous substances (Sindhu et al., 2017). The composition and content of these constituents vary according to the type, variety, and origin of the lignocellulosic material (Abdul Khalil et al., 2016). Most lignocellulosic biomass is composed of approximately 10–25% lignin, 20–30% hemicellulose, and 30–50% cellulose (Fortunati et al., 2016). Lignocellulosic materials with high cellulose content and little hemicellulose and lignin are suitable raw materials for the production of cellulosic materials. Cellulose molecules, a major component of plant cell walls, are regularly arranged and assembled in bundles to determine the framework of the cell wall (Fortunati et al., 2016).

Cellulose and lignin in lignocellulosic biomass are surrounded by hemicellulose chains. There are different bonds between cellulose, hemicellulose, and lignin (Rezania et al., 2019). These molecules are mainly held together by hydrogen bonds. In addition to the hydrogen bonding, there are also the chemical bonds between hemicellulose and lignin. This means that lignin isolated from natural lignocellulose always contains a small amount of carbohydrates. The other constituents of lignocellulosic biomass are extraneous constituents, which refer to all the non-cell wall materials. Extractives can be broadly divided into three groups: terpenes, resins, and phenols. The resin contains a minor amount of various non-volatile compounds, including fats, fatty acids, alcohols, resin acids, phytosterols, and lesser-known neutral compounds. Other extracts include low-molecular-weight carbohydrates, alkaloids, and soluble lignin. Despite the fact that they are present in small amounts, extraneous compounds play a very important role in making cellulose resistant to decay and insect attack, as well as preventing pulping and bleaching.

In general, the relative abundance of cellulose, hemicellulose, and lignin is the key factor in determining the feedstock suitability for nanocellulose production (Rezania et al., 2019). During the production of nanocellulose, all these components except cellulose are degraded and removed at various steps using appropriate solvents (Sindhu et al., 2017). Various studies have shown that the composition of these ingredients varies depending on species, types, and sources. In general, the chemical compositions of various types of common lignocellulosic materials are shown in Table 2.1.

Table 2.1: Chemical composition of some common lignocellulosic materials

Lignocellulosic materials	Composition (%)			Reference
	Cellulose	hemicellulose	Lignin	
Sugarcane bagasse	37.2	22.1	26.5	(Imman et al., 2021)
Rice straw	32-47	19-27	5-26	(Lo et al., 2021)
pumpkin stalk	34.04	12.51	15.41	(Nwaezeapu & Agbozu, 2023)
lemon grass	38.66	26.20	9.93	
Oil palm frond	42.67	34.00	22.90	(Kumneadklang et al., 2019)
Pineapple leaf	34-40	21-25	25-29	(Marcos et al., 2013)
Wheat straw	30	50	15	(Lee et al., 2014)
Nut shells	25-30	25-30	30-40	
Switch grass	45	31.4	12	
Empty fruit bunch	41	24	21.2	
Corncobs	45	35	15	
Barley straw	33-40	20-30	8-17	
Oil palm trunk	29-37	12-17	18-23	(Balcha, 2019)
Water Hyacinth	29.4 -33	24.6 - 28.35	18.36 - 23.8	
Softwood stem	45-50	25-30	25-35	(Mattar et al., 2020)
Hardwood stem	40-45	24-40	18-25	
Lotus Leaf Stalk	34.6	19.2	25.4	(Y. Chen et al., 2015)
Agro-wastes				
Garlic straw residues	41	18	6.3	(Kallel et al., 2016)
Sugarcane bagasse	45	30	20-22	(Mahmud & Rahman, 2021)
Teff straw	36.5	29.5	17.5	(Bacha & Demsash, 2021)
Corn stover	39-44.4	22-28	18-22	(Gro et al., 2021)

2.2. Methods of Synthesizing Nanocellulose from Lignocellulosic Biomass

The excellent properties and potential future applications of nanocellulose make the study of nanocellulose extraction from lignocellulosic biomass very attractive. Biomasses such as waste cotton (Z. Wang et al., 2017), sugarcane bagasse (Plengnok & Jarukumjorn, 2020), wheat straw residues (Wulandari et al., 2016), garlic straw residues (Kallel et al., 2016), agricultural waste corn stover (J. Xu et al., 2018), corncob residue (C. Liu et al., 2016), and others have been studied and used as the source of cellulose for nanocellulose production. However, most of these lignocellulosic biomasses are derived from slow-growing and seasonable plants, which could also be used for other purposes. Therefore, in terms of economic and environmental benefits, it is more profitable to produce nanocellulose from fast-growing, non-seasonable plants as well as plants that could be less utilizable for other purposes. Water hyacinth is one of these fast-growing plants and is therefore a more important and promising source for nanocellulose production.

Various extraction methods have been used to obtain nanocellulose with high crystallinity and surface area by breaking up the glycosidic bonds of cellulose molecules (Oun & Rhim, 2016). These methods include mechanical treatment, biological treatment (enzymatic hydrolysis), chemical treatment (acid hydrolysis), and a combination of these methods (Phanthong et al., 2018). All of these processing methods result in different types of nanostructured cellulose molecules with different dimensions, crystallinity, and morphology depending on their disintegration process and starting source (Bhat et al., 2017).

2.2.1. Mechanical Treatment Methods

The mechanical process is the separation of cellulose fibrils by applying high shear forces to cleavage the cellulose fibers along the longitudinal axis using various approaches. These approaches that have been used to obtain cellulose nanofibers (CNF) include high-pressure homogenizations, high-intensity ultrasonic treatments, microfluidization techniques, ball milling methods, cryocrushing, and grinding. These mechanical processes split the cellulose fibers along their longitudinal axis and generate shear forces sufficient to aid in the extraction of cellulose microfibrils. Each cellulose microfibril has no chain folds and can be viewed as a chain of cellulose crystals connected along the length of the microfibril by disordered or paracrystalline regions. High-pressure homogenization results in greater clogging and requires pretreatment to reduce fiber size and prevent clogging. It is quick, effective, continues the process, and the reproducibility of

laboratory results in ease of scale up to industrial scale. Varying pressure may also determine the appropriate degree of defibrillation. However, high-pressure homogenization requires high energy consumption, high throughput time due to homogenization, and an elevated suspension temperature during the process. High-intensity ultrasonic treatment ensures high power output and the efficiency of defibrillation. However, this method creates heat that must be dissipated and a high level of noise. Also, pretreatment to release CNF is required and is only useful on a laboratory scale (Abdul Khalil et al., 2016). In general, the main drawback of all mechanical processes is their high energy consumption. Therefore, mechanical processes should be combined with other pretreatment methods to reduce energy consumption (Phanthong et al., 2018).

2.2.2. Biological Treatment Method

Enzymatic hydrolysis is a biological treatment process that uses enzymes to digest or modify cellulose fibers under mild conditions. Biological treatment is energy-saving, environmentally friendly, more productive, and selective. Microorganisms such as brown, white, and soft rot fungi and bacteria are also used in biological treatments to degrade lignin and hemicelluloses from lignocellulosic material. However, due to the use of enzymes and other microorganisms, biological treatments require long service lives and high costs. Therefore, biological hydrolysis should always be combined with other methods such as mechanical shearing and high-pressure homogenization to result in controlled fibrillation down to the nanoscale and produce cellulose nanomaterial (Bhat et al., 2017).

2.2.3. Chemical Treatment Method

Chemical treatment is the most promising method to produce nanocellulose, especially nanocrystalline cellulose. It is among the oldest and most widely applied techniques for nanocellulose preparation. For the production of nanocrystals, a number of mineral acids were used, including hydrobromic acid (Sadeghifar et al., 2011), orthophosphoric acid (H_3PO_4) (Gan & Chow, 2018), muriatic acid (HCl) (Yu et al., 2013), and sulfuric acid (H_2SO_4) (Beck-Candanedo et al., 2005). The chemical method produces short, rod-shaped nanocrystals with enhanced crystallinity by reducing energy consumption and outperforming other methods. This method includes alkali pretreatment, oxidizing agents, acid hydrolysis, and ionic liquid pretreatment. Among them, acid hydrolysis is the most commonly used method to produce nanocrystalline cellulose due to its mild operating conditions and the good stability of the resulting suspension.

In order to extract CNCs from cellulosic fibers, a process known as acid-induced disruption is typically used in which the glycosidic bonds in the amorphous region are broken down under controlled reaction conditions (Magagula et al., 2022), as shown in figure 2.2. A number of potent acids have been used to effectively breakdown bulk cellulose and release CNCs, like sulfuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), and a mixture of organic and mineral acids (Mariano et al., 2014). (Risite et al., 2022) compared the effect of three different acids (H_2SO_4, H_3PO_4, and HCOOH/HCl) on the extraction of CNCs from tomato plant residue to form sulfated CNCs, phosphorylated CNCs, and phosphonated CNCs, respectively.

The manufactured CNCs had large aspect ratios (up to 98%), high crystallinity (89%), and produced stable suspensions in organic solvents compared to CNCs that have previously been reported by other sources. To increase thermal stability and synthesis conditions, Raza et al. (2022) attempted to add phosphate groups to CNCs by adding phosphoric acid hydrolysis. Their findings demonstrated that using phosphoric acid medium to produce CNCs reduced the degradation temperatures, but the thermal stability was still on par with that of CNCs made from other biomasses that had undergone H_3PO_4 and H_2SO_4 treatment.

When compared to other acids, the acid hydrolysis process using H_2SO_4 to prepare CNC has received extensive research and appears to be used frequently. This is due to the fact that H_2SO_4 produces stable CNC suspensions and has been shown to be efficient in removing the amorphous components of cellulosic fibers. Due to the reaction between the surface hydroxyl groups of the cellulose and sulfuric acid hydrolysis, which results in the formation of ionic sulfate groups on the surface of the extracted CNCs (Mariano et al., 2014). These anionic sulfate groups cause CNC molecules to repel one another electrostatically and aid in the dispersion of those molecules in water (Homogenization, 2018). Sulfate groups, however, compromise the thermal stability of CNCs and could lead to lower yields. By dialysis-neutralizing the CNCs, the thermal stability of the sulfuric acid-prepared CNC can be improved (Alves et al., 2013). Overall, the acid hydrolysis technique is straightforward and effective for removing CNC from a variety of agricultural residues.

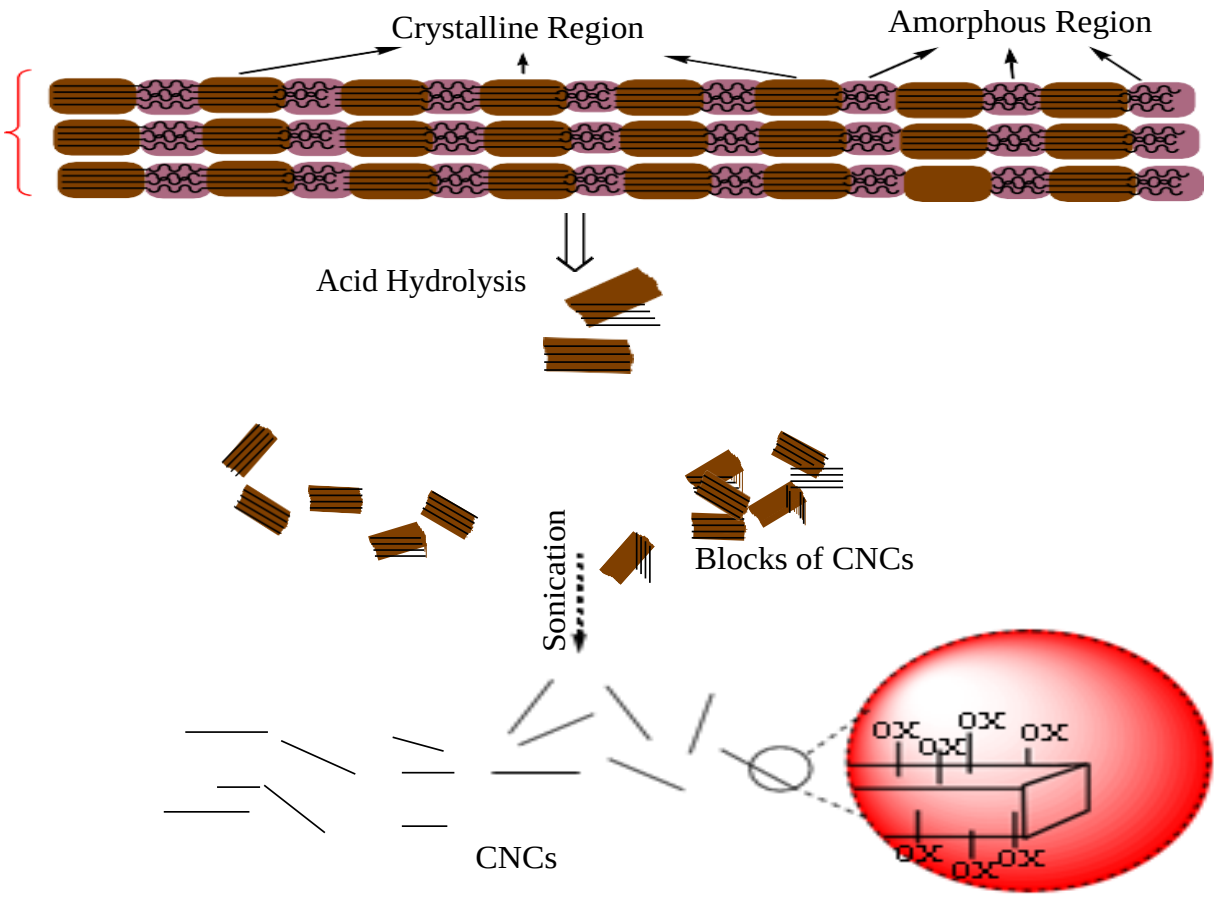


Figure 2.1: Schematic representation of CNC formation from cellulose acid hydrolysis (Le Gars et al., 2020)

Where X depends upon the type of acid used for hydrolysis, for example, in the case of sulfuric acid-induced hydrolysis, X will be SO_3^-; similarly, the value of X will be COO^- and $H_2PO_3^-$ in the case of oxalic acid and phosphoric acid-induced hydrolysis, respectively.

Amorphous domains that are regularly distributed along the cellulose fibers can be destroyed during acid hydrolysis. Strong acids readily penetrate the lower-order amorphous regions and hydrolyze them under controlled conditions without affecting the crystalline regions. Nanocellulose extraction from lignocellulosic biomass by chemical processes consists of two main steps. First, non-cellulosic components, such as lignin, hemicellulose, and other extractive components, are removed by various pretreatment methods. Nanocellulose is then extracted from cellulose fibrils by acid hydrolysis (Bhat et al., 2017; Phanthong et al., 2018).

Table 2.2: Advantages and disadvantages of different acid hydrolysis methods for synthesis of cellulose nanocrystals (CNCs).

Type of acid	Advantages	Disadvantages	References
Hydrochloric acid (HCl)	• Produces CNCs with better thermal stability	• Agglomeration of CNCs occurs	(Bai et al., 2009)
Sulfuric acid (H_2SO_4)	• Easily isolate CNCs • Formation of a stable CNCs • Rapid depolymerization	• Water consumption • equipment corrosion • Yields (15 - 50%)	(Nang An et al., 2020)
Phosphoric acid	• Higher thermal stability of phosphorylated CNCs than Sulfated-CNCs and shows better dispersions.	• Prepared CNCs have a comparable greater size than sulfuric acid-treated fibers	(Gan & Chow, 2018)
Oxalic Acid	• Non-toxic • High yields (71–93%) • Cheap method	• Poor dispersion stability in solvent	(W. Wang et al., 2020)
Oxalic acid Dihydrate	• Simple procedure • Less time-consuming • Low cost of production •Environmentally friendly	• Results in CNCs of low crystallinity index • Poor dispersibility	(W. Xu et al., 2017)
Phosphotungestic Acid	• Higher yield • Acid can be recycled	• Low efficiency • Lengthy process	(Torlopov et al., 2017)
Sulfuric /oxalic acid mixture	• Enhances yield up to 70%. • Results higher thermal stable CNCs and better dispersion ability of CNCs	• Results in lower thermal stability raw cellulosic materials	(Xie et al., 2019)
Sulfuric/acetic acid mixture	• Excellent dispersibility of CNCs and results thermally stable CNCs than acetic acid treated one.	• % Yield decreases with increase in hydrolysis time.	(H. Wang et al., 2020)

2.2.4. Electrospinning

A typical electrospinning setup uses a polymer solution (or polymer melt) to spin continuous fibers under an electric field. Under high voltage, the solution or melt deforms due to repulsion, such as the charge on the surface of the droplets. When the charge repulsion overcomes the surface tension of the polymer, fine jets are then ejected into the collector, and nanocellulose is formed. Electrospinning can produce nanocellulose in the form of non-woven fiber mats or oriented fiber strands, depending on the collector configuration; fiber diameters range from single-digit nanometers to micrometers (Moon et al., 2011).

2.2.5. Bacterial Biosynthesis

Bacterial nanocellulose (BNC) is made by a specific bacterial biosynthesis process that converts low-molecular-weight sugars into cellulose molecules. The generated cellulose molecular chains are excreted into the aqueous culture medium in the form of fibers, which are combined into ribbons and finally into a 3D nanofiber network. A simple purification process can remove all the contaminants, leaving only pure cellulose fibers with nanometer diameters.

2.3. History and Methods of Nanonitrocellulose Synthesis

Similar in appearance to cotton, nitrocellulose is white in color and has a fibrous texture that is made from cellulose. In general, homogeneous or heterogeneous processes are used to produce cellulose nitrates from a variety of cellulose sources, including cotton, wood, and the ever-expanding range of alternative plant-based feedstocks (Sabatini & Johnson, 2021). To understand the chemistry of nitrocellulose, we have to take a look at its parent polymer, which is cellulose. Cellulose is a polysaccharide composed of hundred to ten thousand D-glucopyranose units linked by β (1→4) bonds (Hara et al., 2012). This molecule is a natural polymer that reacts with nitric acid to produce a nitrocellulose ester polymer called nitrocellulose or cellulose nitrate. The precursor (cellulose) and the final product (nitrocellulose) have similar structures, but some hydroxyl groups are modified with nitro groups. When cellulose is nitrated using nitrating mixtures, the hydrogen atom of the (-OH) hydroxyl is substituted for the ($-NO_2$) nitro group. By altering the nitrating mixture composition and nitration process parameters, nitrocellulose with a broad range of functional properties can be synthesized (Mattar et al., 2020). Understanding the nature of the reaction and the variables influencing its rate and extent is necessary to create an empirical kinetic model for the nitration of cellulose in technical mixed acids.

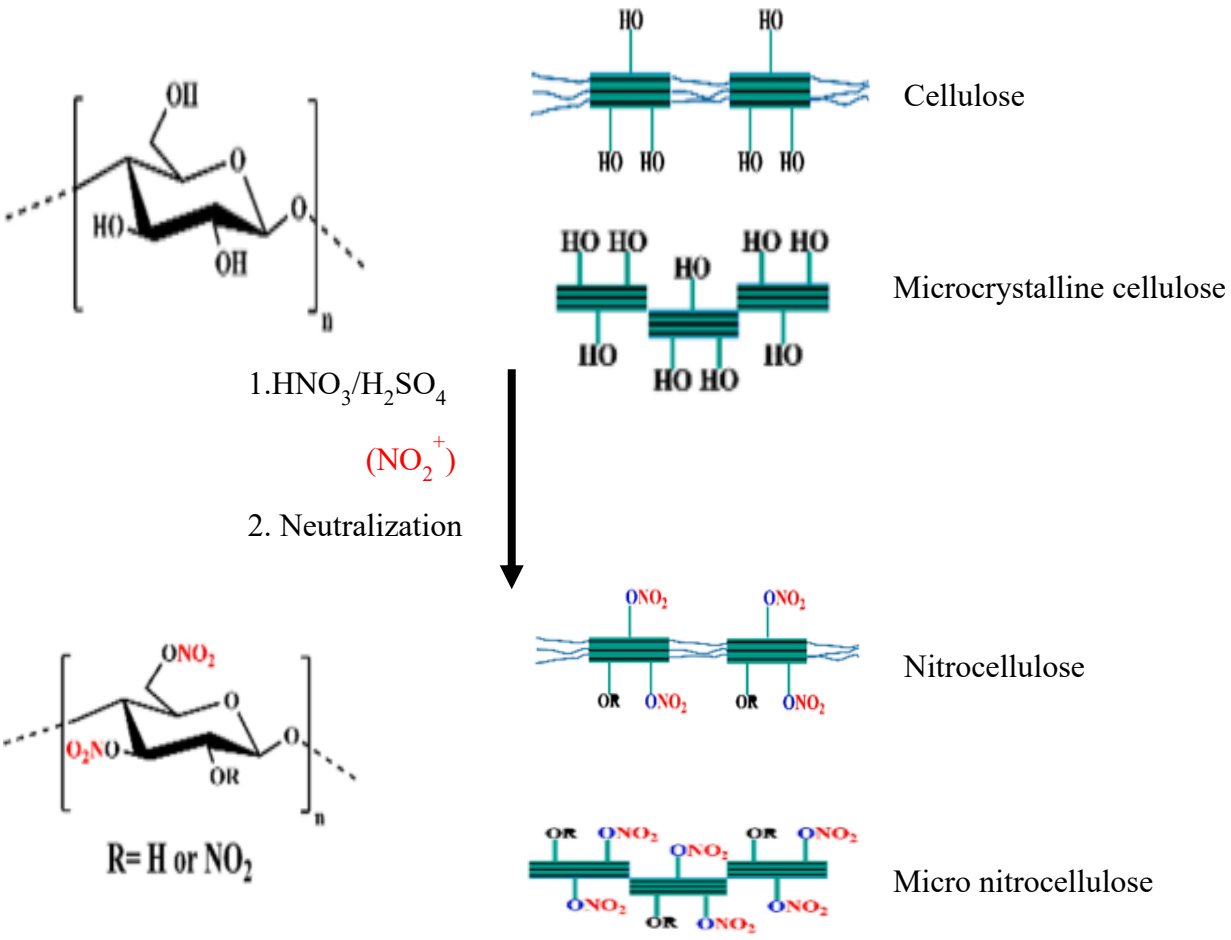


Figure 2.2: General schematic representation for nitration of cellulose and microcellulose (Krumm et al., 2021)

The source, background, and crystallinity of cellulose have an impact on the mechanical, physicochemical, and microstructural characteristics of the nitrocellulose that is produced (Princi et al., 2008). It is commonly known that cotton or wood are the primary raw materials used to make nitrocellulose. With so many industrial applications, it will be interesting to investigate alternative sources for the synthesis of nitrogen-rich polymers. In comparison to fully synthetic thermoplastic elastomers, cellulose is a more advantageous energetic polymer precursor due to its easy and inexpensive availability, renewable nature, biodegradability, lack of pollution, environmental friendliness, and high oxygen content (Li et al., 2017). However, the use of nitrocellulose in some applications, such as gas generators, explosive binder, fireworks, propellant, and pyrotechnics, has been restricted due to its low density, low lubricity, high friability, brittleness

at low temperatures, and shock sensitivity (Betzler et al., 2011). Over the past ten years, significant efforts have been made to create new cellulose-based energetic materials in an attempt to address these shortcomings. The first adopted approach was to introduce energetic chemical groups to get new energetic polymers such as 1-azido-2-hydroxypropyl cellulose ether, butyl nitraminocellulose, methyl nitraminocellulose, cellulose acetate nitrate, azido deoxy cellulose, and azido deoxy cellulose nitrate (Pourmortazavi et al., 2015). Another approach concerns a structural modification of the nitrated cellulose (Walker, 2006).

There is currently a growing need for research on the possibility of producing new nitrocellulose types with tunable functional properties starting from alternative raw sources due to the shortage of conventional cotton resources (J. Liu, 2019). The list of other lignocellulosic sources of cellulose that are not cotton based is constantly growing. Research carried out in certain nations has indicated that it is feasible to produce nitrocellulose with acceptable qualities using cellulose extracted from various sources, including giant reed (A. F. Tarchoun et al., 2020), tobacco (Nicotiana tabacum) stalks (Muvhiiwa et al., 2021), giant panda feces (Duan et al., 2023), intermediate flax straw (Gismatulina et al., 2016b), oat hulls (Korchagina et al., 2019), and Miscanthus cellulose (Gismatulina et al., 2018).

A lot of researchers compare the properties of alternative cellulose with the requirements for cotton cellulose, which calls for a minimum of 92% α-cellulose content. The above-listed studies on nitration differ in their focus. Some researchers only reflect nitration process conditions and specify one of the properties of the resultant nitrocellulose, basically the NC degree of substitution (Jamal et al., 2021; Muvhiiwa et al., 2021), while others report extensive information including basic functional, supramolecular, morphological, and energetic characteristics of the biopolymers synthesized from a specific feedstock type (A. F. Tarchoun et al., 2021; A. F. Tarchoun et al., 2020; Duan et al., 2023; A. F. Tarchoun et al., 2019).

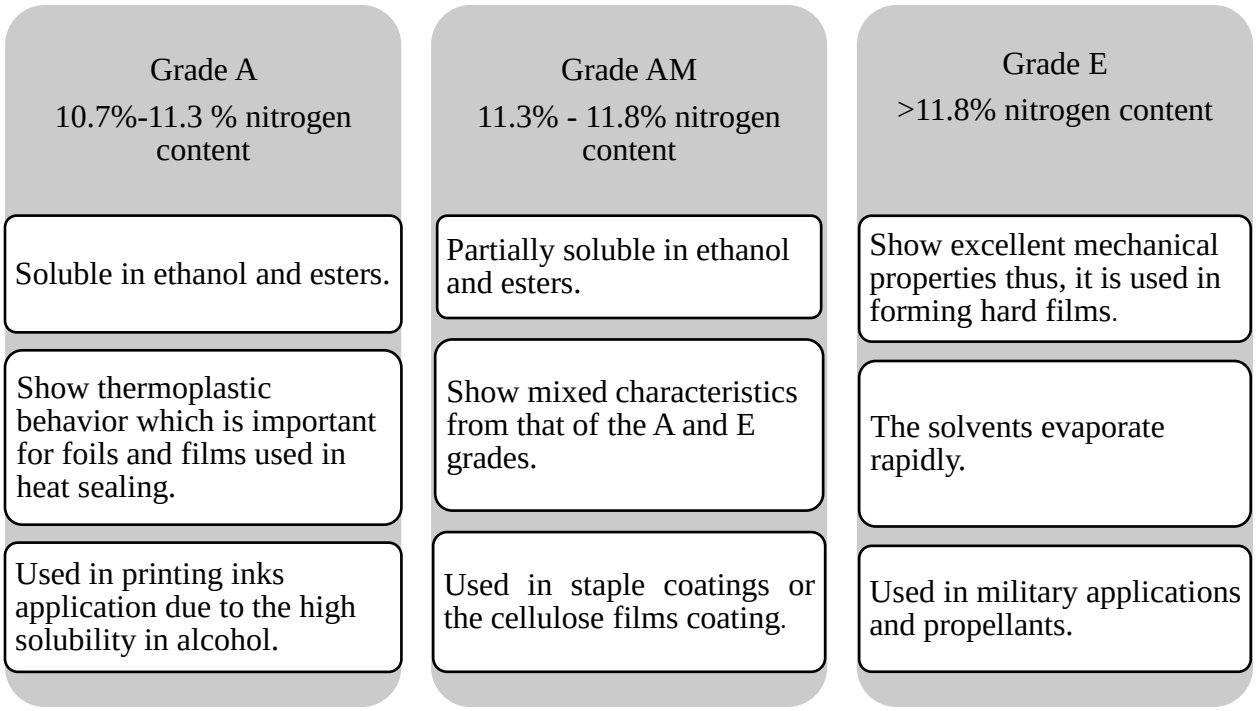


Figure 2.3: classification of nitrocellulose based on their nitrogen content (Mattar et al., 2020)

The French chemist and pharmacist H. Braconnot developed the first nitrocellulose in 1832. By treating cotton or wood pulp (crude cellulose) with concentrated nitric acid (85%, v/v), he created an unstable and flammable solid. The result of this process was xyloidine, an unstable and heterogeneous material. It was distinguished by having a low nitrated cellulose (maximum nitrogen content of 4-5%). Braconnot discovered the forerunner of nitrocellulose, but Schonbein created, 14 years later, nitrocellulose as a stable product. This German-Swiss chemist achieved and patented it by reacting cotton with a mixture of nitric acid and sulfuric acid. Today, this method, with a few variations, is used to produce commercial nitrocellulose. Regarding the method by which nitrocellulose is obtained, as mentioned above, heterogeneous and unstable nitrocellulose with a low nitrogen content was obtained when concentrated nitric acid alone was used. The synthesis process was improved by adding nitric acid vapor as a pretreatment, prior to the addition of 98% nitric acid. In this case, the vapor phase helped to produce stable and homogeneous nitrocellulose with a high degree of nitration (nitrogen content ≈13.6%). Reaction of cellulose with a mixture of nitric and sulfuric acid also allowed to obtain a stable product with a high degree of nitration (nitrogen content of 13.9% as maximum, and the best proportion of these two acids was demonstrated to be 1:1 to 1:3 (nitric acid: sulfuric acid) (García-ruiz, 2012).

A mixture of nitric and phosphoric acid in the ratio of 1:1 to 1:3 (nitric acid: phosphoric acid) produced nitrocellulose with a nitrogen content of up to 13.7%. The final product was highly stable nitrocellulose, but phosphoric acid corrodes iron and steel, and there were problems in the production of nitrocellulose. Nitrocellulose with a nitrogen content of up to 14% can be produced by mixing nitric and acetic acids (García-Ruiz, 2012). The main drawback of this reaction was the appearance of acetyl nitrate in the reaction medium, which is a very unstable substance at high temperatures.

Another method of producing nitrocellulose was to use nitric acid and organic solvents, such as carbon tetrachloride, methyl nitrate, or chloroform, which produced nitrocellulose with a high nitration degree (nitrogen content up to 13.4%) and high yields (García-ruiz, 2012).

Table 2.3: Methods of nitration for synthesis of nitrocellulose (Fernandez de la Ossa et al., 2011)

Nitrating agents	Maximum nitrogen content (%) attained	Observed gaps and comments
Nitric acid only	✓ 8% ✓ 13.6% - 13.8% when treated with vapor first.	✓ gelatinization of surface fibers upon contacting the acid. ✓ No Industrial use so only done in labs
Nitric Acid, Sulfuric Acid, and water	✓ 13.92%	✓ Decreasing water induces swelling and reduces the rate of the reaction and increasing water decreases the nitrogen content ✓ generates a large amount of waste acid and by-products, and requires a laborious procedure for the stability treatment.
Nitric acid and Phosphoric acid	✓ 13.7%	✓ phosphoric acid corrodes iron and steel. ✓ Deviation away from the composition of the nitrating mixture had an effect of crystallizing or hardening the fibers.
Nitric acid and acetic acids/acetic anhydride	✓ ≥14	✓ The potential formation of acetyl nitrate (explosive at high temperatures)
Nitric acid and organic Solvents (Carbon tetrachloride, methyl nitrate, or Chloroform)	✓ 13.4%	✓ The polymer chain was not degraded by the nitration process which leads to improved mechanical properties

Nowadays, producing nano- or micro-scale energetic materials is the best method for increasing the amount of energy release, ignition, and combustion behaviors of energetic materials (Rossi et al., 2007). In most cases, combustion reactions are basically constrained by a specific surface area. With a decrease in particle size, more molecules are displayed on the surface, which increases the free surface energy and specific surface area and subsequently improves the combustion reaction. Therefore, the burn rate of nano- or micro-scale materials is significantly faster than that of macro-scale bulk materials and offers higher energy release and more complete combustion than the bulk one.

Energy-dense nanomaterials can enhance thermodynamic characteristics like melting point and decomposition temperature, which are advantageous for quick breakdown and total combustion (or explosion), hence improving their efficiency with energy. According to studies, nano-energetic materials have the potential to offer a number of performance benefits, such as increased mechanical properties of explosives, reduced sensitivity, high energy release rates, and outstanding combustion (energy conversion) efficiency (Xia et al., 2012). With a nitrogen content of 11–13.5%, nitrocellulose is a crucial raw material that is widely used in explosives and propellants. Cotton balls with a fiber diameter of 40–50 μm make up traditional NC balls. It displays limited thermoplasticity as a propellant adhesive since it is a typical semirigid chain polymer material. It is harder for NC with a high nitrogen content, in particular, to be absorbed by the nitrate plasticizer. This makes the propellant molding process more challenging and leads to a product with poor mechanical properties (J. Liu, 2019). The conversion of traditional NC to fiber nanometers can result in nano-sized NC fiber with a higher specific surface area, making it more suited for absorption by nitrate plasticizer. Meanwhile, NC-based explosives can function better thanks to nano-sized NC fiber, which can enhance NC combustion and energy conversion efficiency.

For nitrocellulose, researchers have been carrying out much research in the field of its modification and synthesizing some materials with new properties (Sovizi et al., 2009a). But the insensitive research on nitrocellulose has not received enough attention in the past. Current insensitive studies of energetic materials have concentrated primarily on explosives, and many technologies of desensitization for high explosives are being developed (Yang et al., 2023). The physical characteristics, such as crystal quality, morphology, and size, of high-energy explosives can affect their sensitivity to accidental stimuli. Many studies have shown that reducing the crystal lattice

defects in energetic materials helps to reduce their sensitivity (Ma et al., 2020). In addition, the energetic materials with the highest sphericity and the smallest size also have lower sensitivities (Shi et al., 2014). In addition, reducing the particle size of energetic materials has some other benefits. For example, reducing the ingredients of propellants to nanoscale dimensions can lead to increased combustion rates and a significant efficiency improvement (Zohari & Keshavarz, 2013). Therefore, a possible method to reduce the sensitivity of nitrocellulose is to improve its crystal quality and morphology and reduce its size as well.

Recently, studies on nitrocellulose to improve its environmental suitability, cost, thermal stability, and sensitivity have been reported. Some research has focused on fabricating nitrocellulose from materials other than wood and cotton. Nanosized spherical NC composite crystals (diameter = 15 to 30 nm) were obtained through the pretreatment, hydrolysis, and nitration of microcrystalline cellulose. The shock sensitivity of the nanosized spherical NC decreased by 44.6% compared to that of traditional nitrocellulose (Okada et al., 2021).

(Q. Wang et al., 2023) used the electrospinning (ES) approach to prepare thermite-based nitrocellulose nanofibers. Nanothermite in the nitrocellulose polymer matrix significantly increased the total energy released and the combustion propagation rate. Similarly, (Sovizi et al., 2009a) prepared two different types of nitrocellulose nanofiber (diameter: smooth nanofiber = 90-150 nm, diameter: porous nanofiber=400-500 nm) by electrospinning an ethyl methyl ketone solution. In another study, organic solvent – soluble nitrocellulose was deposited on a glass substrate and dried to yield particulate nitrocellulose (diameter = 200-900 nm). In addition, nanosized nitrocellulose has attracted attention because it is more reactive than micron-sized nitrocellulose. (Zhang & Weeks, 2014) also prepared submicron nitrocellulose particles (diameter = 500 nm) using dimethylformamide (DMF) solvent, resulting in nitrocellulose with a higher burning rate.

The electrospinning and dropping methods have several limitations, as listed below (a–d). (a) The diameter of nitrocellulose produced by the electrospinning method ranges from 90 to 500 nm, and its specific surface area ranges from 4.8 to 26.9 m^2/g. Therefore, it is not possible to prepare NC nanofiber (NCNF) with a diameter of 50 nm or less and a specific surface area of 80 m^2/g or more by this method. (b) In the electrospinning method, the manufacturing process needs high voltage. Therefore, a safety counterplan is necessary to reduce explosion risks. (c) In the electrospinning

method, it is necessary to dissolve nitrocellulose in the solvent before spinning, and a special solution is required. But, NC with low nitrogen content is difficult to dissolve; thus, it is difficult to produce NC with different degrees of nitration to suit different applications. (d) The dropping method is not suitable for mass production because the dropped volume is too small. Moreover, the specific surface area of the fabricated nitrocellulose was only 4.0 to 18.2 m^2/g. An aqueous suspension of cellulose nanofiber (CNF) was used as a raw material for nanonitrocellulose. To the knowledge of the authors', this has not been used for this purpose in the past. The aqueous suspension of CNF was pretreated with sulfuric acid before esterification to promote the swelling of CNF and increase the nitrification rate.

With nanocrystalline cellulose (NCC) as the starting material for nitrification, it is possible to improve the already existing material made from bulk cellulose. The use of NCC has several advantages over nitrification. Firstly, the NCC purification process involves the delamination of and selective removal of hemicellulose and lignin. Hemicellulose cannot be nitrified to the same extent as the cellulose branching of the polymer removes reactive OH groups (Granström, 2009). Similarly, the polyaromatic lignin, upon nitrification, does not contribute positively to the amount of nitrogen in the overall product. The presence of such non-cellulosic nitrated products leads to differences and uncertainties in determining the quality of the nitrated product. Secondly, the increased crystallinity and order of nanocrystalline cellulose can improve the homogeneity of nitrification (Cheung, 2014). Without the amorphous regions containing large variation in chain length in the cellulose polymer, regions with high crystallinity represent a narrower molecular weight range, and hence the distribution of the nitrogen content of the product can ultimately be better controlled to produce a nitrated product with better chemical properties. Thirdly, due to the shorter polymer chain length, the number of glucosidic terminating groups in NCC increases. While the average monomer in cellulose has a maximum of three reactive OH radicals for electrophilic substitution, the terminal groups contain four up to five reactive OH groups, depending on whether one considers the pyranose form or the open linear form of glucose, which are also available for nitration (Habibi et al., 2010). Thus, a nitrification product with a nitrogen content higher than the theoretical maximum of 14.1% of nitrogen can be obtained.

2.3.1. Degree of Substitution

The nitrogen content of nitrocellulose, or the mass percent (N%) of nitrogen found in the nitrocellulose molecule, can be expressed as a degree of nitration or degree of esterification. The nitration degree (NO, ml/g) is the volume of released nitric oxide (NO) when the decomposition of one gram of nitrocellulose is completely done in the standard conditions (0 °C,1atm).The degree of substitution (DS) designates the quantity of hydroxyl groups exchanged and can be calculated by the following equation (García-ruiz, 2012).

$$Degree\ of\ \ substitution\ (DS) = \frac{3.6 \times nitrogen\ content\ (\%)}{31.13 - nitrogen\ content\ (\%)} \tag{2.1}$$

DS is one of the most important properties of nitrocellulose, as it influences other properties such as solubility and viscosity and determines the applications of nitrocellulose. The lowest DS value is 1, indicating a nitrogen content of 6.76% in the nitrocellulose monomer. The highest DS value is 3; it means that all the hydroxyl groups are replaced with nitro groups, producing a theoretical nitrogen content of 14.14%. However, the maximum DS actually achieved was 2.9, which is a polymer with a nitrogen content of nearly 13.9% (Torre, 2012) because the synthesis of these highly nitrated products is costly and hazardous due to unstable product formation. The density of nitrocellulose increases with increasing nitrogen content (He et al., 2017). The solubility and viscosity of nitrocellulose is directly affected by the degree of substitution (Torre, 2012).

The intrinsic viscosity increases the degree of polymerization (Mattar et al., 2020). The higher the degree of polymerization, the higher the increase in intrinsic viscosity with increasing nitration observed. But cellulose derived from different sources and having different degrees of polymerization, nitrated to the same level, may have significantly different viscosities intrinsic to each other. Solubility decreases as the nitrogen content decreases. Thus, although low-nitrated nitrocellulose (DS of 1.9–2.1) is soluble in alcohols, esters, ketones, and glycol ethers, high-nitrated nitrocellulose (DS of 2.1–2.4) is insoluble in formulations of alcohol, although it may be dissolved in esters, ketones, and glycol ethers. In comparison to solubility, as the nitrogen content of nitrocellulose and the concentration of nitrocellulose solutions increases, the viscosity increase accordingly (Mattar et al., 2020).

2.3.2. Applications of Nanonitrocellulose

2.3.2.1. Military Applications

Nitrocellulose, with a high nitrogen content of 12.95%- 13.35%, is commonly referred to as gun cotton to describe how this material is explosive and highly flammable (Abdelaziz et al., 2022). NCs are often found in gun powders, which are usually classified by the number of energetic materials in their formulation: (I) single-base propellants containing predominantly NC; (II) double-base propellants consisting of NC and nitroglycerin; and (III) triple-base propellants containing NC and two other explosives (nitroglycerin, dinitroethylenglycol, and nitroguanidine). There are different types of explosives; one of these is dynamite (which is an explosive mainly for civil purposes); another is a propellant, most commonly known as gunpowder (which is an explosive utilized to move projectiles at rapid speeds) (Torre, 2012). It is continuously developed to improve its properties, such as stability and burn rate. Researchers have developed an improved sub-micron nitrocellulose manufacturing technique that yields particles with low activation energy for the decomposition process, a greater increase in its burn rate by 350%, and the characteristics to achieve complete combustion (Q. Wang et al., 2023). In order to increase the burning rate of nitrocellulose, another study was done to study the effect of doping nitrocellulose microfilms with graphene oxide (GO) in the range of 0.5-3 wt% (Deng et al., 2021).

Another method is to catalytically change the macrostructure and modify the geometry of the shape itself. A flammable solid composite propellant, AP-NC (Ammonium Perchlorate Nitrocellulose), had its flammability increased by a magnitude of 7 times, and its activation energy decreased by 25%. This was made possible using three-dimensional, highly conductive, interconnected, porous, and CuO (copper oxide)-functionalized GF (graphene foam) microstructures. The graphene foam structure itself distributed and conducted the heat more efficiently than without it, thus increasing the burn rate. The addition of CuO acted as a catalyst for the burning yet had a negative effect as well; as it needed some of the exothermic energy to get heated up. An optimum loading of both GF and CuO was determined at 10% and 3%, respectively (Jain et al., 2019).

2.3.2.2. Medical Applications

Nitrocellulose has proven to be very beneficial and versatile in the medical field. It simplifies previously cumbersome operations, increases the accuracy and efficiency of examinations, and provides several new techniques for detecting changes in the human body. First, nitrocellulose is

widely used and studied in biosensor and chip applications that can detect various antibodies, proteins, serums, and other chemicals that affect body homeostasis. Nitrocellulose can be used as an adsorption layer for the sensor chip of the MCLW (metal clad leaky waveguide) optical biosensor. This should enable label-free detection of the CRP (carbon reactive protein) in human serum and for immobilization of the antibody on the chip (Bae et al., 2014). Allergies and allergenic chemicals are areas where nitrocellulose is also being researched. The test commonly used to look for allergies and find their triggers is the radioactive allergy test (RAT), which usually uses cyanogen bromide activated paper, although nitrocellulose sheets are more effective in research.

The properties and characteristics of such films and membranes can also be improved by various techniques. Polysaccharides (both bacterial and neutral) adhered to nitrocellulose in a novel technique called vacuum filtration. The resulting films can be used as blotting assays to study specific types of antibodies. The simplicity, rapidity, and efficiency of the process itself make it a great advantage and a great prospect (Mattar et al., 2020). Due to their high protein binding affinity, compatibility with various detection techniques, and the ability to immobilize proteins and glycoproteins, nitrocellulose membranes are a popular matrix used in protein blotting. Nitrocellulose membranes can also be used for southern and northern blots, amino acid analyses, western transfers, and dot/slot blots. Nitrocellulose membranes have a protein-binding capacity of 80 to 100 $\mu g/cm^2$. Protein immobilization is believed to occur through hydrophobic interactions during electrophoretic transfer. High salt concentrations and low methanol concentrations promote protein immobilization on the membrane, especially for high-molecular-weight proteins. Due to the high efficiency of irreversible protein binding, nitrocellulose membranes remain a common option.

2.3.2.3. Industrial Applications

In addition to the medical field, NC is now also widely used in wood coatings, which are coatings and lacquers used to improve the ascetic properties of wood products, improve the surface finish, and extend the lifetime and service life of the product. Companies with this concept use quick-drying syst combined with nitrocellulose resins, and such NC abrasive sealers and NC varnish have been introduced for interior house and office furniture. For either the sealing application or the varnish application, a 20% solution of NC is used, and it is 50 wt% of the lacquer (Mattar et

al., 2020). The lacquer was unique for its high mechanical strength, hardness, and transparency, as well as its very fast drying time.

2.4. Summary of Related Works on the Synthesis of Nanonitrocellulose

Various investigations have been carried out for the synthesis and characterization of nitrocellulose. Nitrocellulose has attracted great interest from researchers because it is used in a wide range of products, including paint and gun propellant. (Hasnawati et al., 2020) focus on the synthesis of nitrocellulose from bacterial cellulose by nitration. Experiments were performed at different reaction times: 30, 60, and 90 min. Then nitrocellulose with a nitrogen content of 12.1% was obtained with an optimum reaction time of 60 min. Similarly, (Gismatulina et al., 2019) studied the scale -up production of an enlarged BNC (bacterial nanocellulose) sample and the synthesis of cellulose nitrate (CN) therefrom. The most representative BNC sample, with a weight of 6800 g, an α-cellulose content of 99%, and a polymerization degree of 4000, was nitrated. Nitration of freeze-dried BNC was performed with sulfuric-nitric mixed acid and nitrocellulose, with a nitrogen content of 10.96% and a viscosity of 916 cp.

(Adekunle, 2010) studied a method to produce cellulose nitrate polymer from sawdust of Nigerian origin using a method that involved alternative alkali and chlorination treatments to remove non-cellulosic components, followed by a nitration reaction. The effects of nitrating acid mixture type and composition, nitration time, and ratio of nitrating acid mixture to cellulose material on yield and solubility of products were investigated. The results showed that variations in the composition of the particular nitrating acid mixture, the relative acidity of the nitrating mixture, nitration time, and the ratio of nitrating acid to cellulose material all influenced the yield and solubility of cellulose nitrate, whose nitrogen contents ranged from 11.06 to 13.12%.

(Okada et al., 2021) have developed a new process for the manufacturing of nanoscale nitrocellulose (NC). Aqueous suspensions of cellulose nanofiber (CNF) were obtained by disk-milling cotton powder. CNF was first pretreated with sulfonic acid to enhance the esterification process using HNO_3 and H_2SO_4. The esterification process produced nitrocellulose nanofiber (NCNF) with a nitrogen content between 9.0% and 13.7%. The Brunauer-Emmett-Teller (BET) specific surface area of NCNF was 10 times higher than that of NC, and the burning rate of NCNF was 3.5 times faster than that of NC. On the other hand, (Zhang & Weeks, 2014) presented a new method to generate spherical sub-micron nitrocellulose particles.

The morphology of the nitrocellulose can be controlled by the solvent and the growth temperature. Spherical nitrocellulose particles were reproducibly obtained using dimethylformamide (DMF) at a growth temperature of 5 ℃. The final diameter of the prepared nitrocellulose particles can be further tuned by concentration. The smallest particles in this study were found to be 2-micron spheres formed at 30 mg/ml with a diameter of 500 nm at a concentration between 5 and 10 mg/ml. Additionally, the thermal properties and burning kinetics of the prepared materials were investigated by differential scanning calorimetry and digital high-speed photography, respectively. Compared to the bulk nitrocellulose material, the sub-micron nitrocellulose particles have a lower decomposition activation energy, a 350% increase in burn rate, and more complete combustion.

(Gismatulina et al., 2016a) also published the first findings on the synthesis of cellulose nitrates from oilseed production residues (intermediate flax straw) for the first time. Cellulose was isolated by the dilute nitric acid method, and cellulose nitrates were synthesized using an industrial sulfuric -nitric acid mixture. It was found that cellulose nitrates with the following properties can be obtained from the intermediate flax straw: weight fraction of nitrogen 12.23%- 12.34%, viscosity 2.7- 16.0 cp, and solubility in an alcohol -ether mixture 95% –96%. (Gismatulina & Budaeva, 2017) also explored the possibility of synthesizing nitrocellulose (NC) from a readily renewable non-woody feedstock, Miscanthus. Nitration of Miscanthus cellulose with a commercial mixed acid has been shown to yield high-quality NC with 11.85% nitrogen content, 18 cp viscosity of 2% NC-acetone solution, 97% solubility in alcohol-ester mixture, and 0.11% ash content. A novel nano-sized spherical NC composite crystal based on the pretreatment, hydrolysis, and nitration of microcrystalline cellulose was prepared by Meng et al. (2020), and its diameters are in the range of 15-30 nm with 14.89% nitrogen content.

Nitrocellulose (NC) is useful in several industrial fields, especially in the production of propellants for guns, rockets, and missiles. The conventional way to prepare NC is through the nitration of plant cellulose with nitric acid. (Hasnawati et al., 2020) synthesized bacterial cellulose nitrate (NBC) by bacterial cellulose (BC) and nitric-sulfuric acid under heterogeneous conditions. NBC with a degree of substitution (DS) of 1 -2.85 was obtained, and the effects of sulfuric to nitric ratio, reaction temperature, and reaction time on the value of DS of NBC were investigated. It is well known that the raw materials used to make nitrocellulose are usually wood or cotton. It is of interest to explore other sources for the synthesis of nitrogen-rich polymers. Despite the topicality of

research on NC synthesis, including that from non-woody raw materials and bacterial cellulose, there is no account on the synthesis of NC from water hyacinth. In this respect, the present work aims to utilize this plant for the extraction of cellulose nanocrystals (CNCs) and synthesizing nanostructured nitrocellulose.

Table 2.4: Review summaries of some of the related works on the synthesis of nanonitrocellulose

Cellulose source used for nitration	Methods used	Content of nitrogen (%)	Reference
Bacterial cellulose	Mixture of H_2SO_4 and HNO_3	12.1	(Hasnawati et al., 2020)
Sawdust	- HNO_3/H_2SO_4 -HNO_3/H_3PO_4 - HNO_3/Ac_2O	11.06 to 13.12%	(Adekunle, 2010)
Cotton	Mixture of H_2SO_4 and HNO_3	9.0% to 13.7%	(Okada et al., 2021)
Cotton based CNF	Mixture of CH_3COOH, Ac_2O, and HNO_3	6.1%	(Saito et al., 2023)
Microcrystalline cellulose	Mixture of H_2SO_4, H_3PO_4, CH_2O_2 or CH_3COOH with HNO_3	12.5%	(Santos et al., 2021)
Intermediate flax straw	Industrial sulfuric - nitric acid mixture	12.23% to 12.34%	(Gismatulina et al., 2016a)
Miscanthus	Commercial mixed acid of nitric and sulfuric acid	11.85%	(Gismatulina & Budaeva, 2017)
Microcrystalline cellulose	Mixed acid of sulfuric acid and nitric acid	14.89%	(Meng et al., 2020)
Cotton	Homogeneous esterification of cellulose by using ionic liquids	12.62%	(Duan et al., 2022)
Miscanthus	Mixture of H_2SO_4 and HNO_3	11.18%	(Korchagin, 2023)
Giant panda feces	Commercial nitro-sulfur mixed acid	12.5%	(Duan et al., 2023)
Microcrystalline cellulose	Mixture of H_2SO_4 and HNO_3	≥12.99%	(A. Tarchoun et al., 2022)

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Chemicals

Raw water hyacinth (WH) was gathered from a local water body (Koka dam) in Ethiopia. The reagents and chemicals used were toluene (C_7H_8, 99%), ethanol (C_2H_5OH, 97%), sodium hydroxide (NaOH, 97%), sodium hypochlorite (NaOCl, 6%), sodium carbonate (Na_2CO_3), distilled water, acetic acid (CH_3COOH, 99.5%), sulfuric acid (H_2SO_4, 98%), and nitric acid (HNO_3, 70%). All the chemicals were analytical grade and obtained from the Ethiopian Defense University Engineering College.

3.1.2. Equipment's/Materials

The equipment and instruments such as miller, Soxhlet apparatus, laboratory test sieve, measuring cylinder, analytical balance, pH meter, water bath, hot air oven, muffle furnace, desiccator, centrifuge, ultrasonicate, freeze dryer, desiccator, Petri dish, vacuum pump, spatula, hot plate, filter paper, Soxhlet extraction setup, magnetic stirrer, vacuum oven, burette, Erlenmeyer flask, round bottom flask, and conical flasks were used in this study. Furthermore, instruments such as the Particle Size Analyzer (PSA), nitrogen content elemental analyzer (Kjeldahl unit), (scanning electron microscopy (SEM), Attenuated total reflection Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), adiabatic bomb calorimetry, and thermal analyzers (TGA-DSC) were used for the characterization of the samples.

3.2. Methods

3.2.1. Proximate Analysis of a Raw Water Hyacinth Sample

The percentage of volatile matter, moisture content, ash, and fixed carbon content of a raw water hyacinth was estimated by Proximate analysis. The procedure for estimating each of those four quantities is based on ASTM standard methods as follows:

Determination of moisture content: The moisture content of the raw water hyacinth was determined by weighing 5 g of a sample into a labeled, pre-weighed petri dish and placing it in an

oven to dry at 105 °C for 3 hours following ASTM E-1756 (Method, 2020). After drying, the petri dish and dry sample were transferred to a desiccator to cool before being weighed again. The percentage of moisture content was calculated by equation 3.1.

$$\text{Moisture content}(\%) = \frac{W_i - W_f}{W_i} \times 100 \tag{3.1}$$

Where W_i is weight before drying and W_f is weight after drying.

Determination of volatile matter: One gram of sample, free of moisture, was placed into a crucible, then placed in a muffle furnace at a temperature of 950 ℃ for seven minutes, and then cooled in a desiccator by using ASTM E-872 (Silva et al., 2021). The percentage of weight loss will give us the volatile matter content, calculated as:

$$\text{VM}(\%) = \frac{\text{loss due to removal of volatile matter}}{\text{weight of sample taken}} \times 100 \tag{3.2}$$

Where VM = volatile matter.

Determination of ash content: Three grams of the dry sample were placed into a crucible. The crucible containing the sample was placed into a muffle furnace at 575 ℃ for three hours following ASTM, E-1755 (Drews, 2008). A temperature of 575 ℃ was chosen due to the fact that carbohydrates (250-350 ℃) and lignin (300 -500 ℃) oxidize at these temperature ranges (Ayeni et al., 2015) Then the ash content was calculated using equation (3.3).

$$\text{Ash content}(\%) = \frac{\text{weight of ash left}}{\text{weight of sample taken}} \times 100 \tag{3.3}$$

Determination of fixed carbon: The fixed carbon was calculated from the expression as follows:

$$\text{FC}(\%) = 100 - \%\text{ of (moisture + volatile + ash) content} \tag{3.4}$$

where FC is fixed carbon.

3.2.2. Chemical Composition Analysis

Determination of extractive content: 3.5 grams of raw water hyacinth were taken, and Soxhlet extraction was done at 70 °C using 150 mL of acetone. After 4 hours of extraction, the sample was

air-dried for a few minutes at room temperature. Dry again in an oven at 105 °C. The difference in weight before and after is the content of extractives (Ayeni et al., 2015).

Determination of hemicellulose content: 1 gram of dried extractive-free WH was transferred into an Erlenmeyer flask. Then 150 mL of 0.5 mol/L NaOH was added and boiled for 3.5 h (Mansor et al., 2019). It was filtered and washed to a pH of 7, and then the sample was dried at 105 °C in a conventional oven. The difference between the sample weight before and after this treatment was the hemicellulose content.

Determination of lignin content: Lignin content was determined according to the method of the Institute of Paper Chemistry, Appleton, Wisconsin, as depicted in Tappi (Tappi, 2011). 1 g of dried extractive-free sample was treated with 20 ml of 72% sulfuric acid by adding the acid drop-wise with consistent mixing. After that, the sample was permitted to stand overnight at room temperature. The sample was transferred to a round-bottom flask, diluted to 3% sulfuric acid, and boiled for 4 hours. The lignin was filtered and washed with hot, distilled water until it became neutral. Then lignin was dried at 105 °C for 6 hours, repeating until a constant weight and lignin content were calculated according to equation 3.5.

$$\text{Lignin}\,(\%) = \frac{M_1}{M} \times 100 \tag{3.5}$$

Where M_1 is the obtained lignin mass and M is the initial sample mass.

Calculate cellulose content (%w/w) by difference. Assume that the material contains only cellulose, hemicellulose, lignin, and extractives.

3.2.3. Isolation of Cellulose

The stems of WH were separated from leaves and roots with a laboratory knife, washed with distilled water to do away with dust, and then dried in an oven at a temperature of 60 °C for 24 hours (Phanthong et al., 2018). The dried sample was milled and sieved at a 250 µm sieve to obtain a powdery sample, which was then sealed in a plastic bag until use. Subsequently, the sample was dewaxed in a Soxhlet apparatus by the use of a combination of toluene and ethanol solvents with a ratio of 2:1 (v/v) at 85 °C for 5 h to cast off extractive additives along with wax, pectin, and oils (Jiang & Hsieh, 2015). The de-waxed powder was washed with distilled water using a 45-µm sieve to get rid of solvent, and finally it was dried in an oven at 45 °C to a constant weight. The dewaxed

sample was treated twice with 4% (w/w) NaOH solutions with a ratio of 1:20 (g/ml) at 80°C for 2 h under consistent agitation at 500 rpm (Achaby et al., 2017). This step was intended to reduce lignin and hemicellulose content and improve nanocellulose synthesis process efficiency. The treated sample was completely neutralized with diluted acetic acid and distilled water. The sediment obtained from centrifugation was then dried in an oven at 45°C to a constant weight.

After alkaline pretreatment, bleaching was done twice by using a mixture of 6% (w/w) sodium hypochlorite solution and acetic acid at a ratio of 4:1 (v/v) under acidic conditions at a p^H of 4 at 80 ℃ for 2 hours with a sample to solvent ratio of 1:20 (g/ml) to remove lignin (Achaby et al., 2017). Then the bleached sample was cooled by adding distilled water to the reactor and washed repeatedly with diluted solution of sodium hydroxide and distilled water until it was free from acid and had a P^H of 7. Subsequent centrifugation was performed by replacing the supernatant with distilled water during washing steps until white cellulose was obtained. Finally, the resulting white cellulose was dried in a vacuum oven to obtain cellulose powder and preserved in a sealed plastic bag for further analysis.

3.2.4. Extraction of nanocellulose

Purified cellulose obtained from water hyacinth was acid hydrolyzed using 10 g of cellulose in 250 ml of sulfuric acid under controlled conditions of 50% sulfuric acid at 60°C for 30 minutes and continuous agitation at 500 rpm using the optimized conditions based on literature (Pantamanatsopa et al., 2023). The hydrolysis process was quenched by adding 400 ml of distilled water to the reaction mixture. The aqueous NCC suspension was neutralized by adding 0.05 M NaOH until the pH of the aqueous CNC solution was neutral and then washed repeatedly by continuous centrifugation at 4000 rpm for 25 min to remove free acid from the dispersion (Pantamanatsopa et al., 2023). The neutral NCC suspension was ultra-sonicated for 15 minutes by using a probe ultra-sonicator at the Leather Industry Development Institute (LIDI), Ethiopia, to obtain a homogenized dispersion called NCC suspension. Finally, the NCC suspension was freeze dried by using a freeze dryer to obtain the suspension in powder form for some characterization, and the yield of dried nanocellulose was calculated by equation 3.6.

$$\text{Yield}\,(\%) = \frac{W_{nc}}{W_o} \times 100 \tag{3.6}$$

Where W_{nc} represents the weight of dried nanocellulose obtained after hydrolysis and W_o is the weight of bleached cellulose used for hydrolysis.

3.2.5. Preparation of nanonitrocellulose

Prior to the nitration of nanocellulose, the isolated cellulose nanocrystal quality was measured by standard analytical methods. The cellulose content was determined by the TAPPI standard by which nanocellulose was treated with a 17.5% (w/w) NaOH solution and the undissolved residue was quantified after being washed with a 9.5% (w/w) NaOH solution and water, followed by drying (Technical Association of Pulp and Paper Industry, 1999). The acid-insoluble lignin content was determined by the TAPPI standard by using 72% H_2SO_4 (Tappi, 2011).

The nano-sized cellulose crystal was nitrated with a mixed acid of sulfuric acid and nitric acid by using H_2SO_4 (98%) and HNO_3 (70%), and esterification was conducted (Okada et al., 2021). A known weight of pre-dried nanocellulose was placed in a conical flask, and the nitrating acid mixture was added via a burette while stirring with a magnetic stirrer. Key parameters of nitrating acid to cellulose ratio (20–30) ml/g, sulfuric acid to nitric acid ratio (2.4–3.6), nitrating time (20–60) min, and nitration temperature (20–40) °C were used, and their effects have been studied based on literature (Korchagina & Budaeva, 2019). At the end of nitration, the nitrated residue was separated by vacuum filtration, and the filtrate was left overnight for maximum reaction, then removed by centrifugation at 1,400 rpm for 10 minutes (Adekunle, 2010). The synthesized nano-nitrocellulose was stabilized by sequential treatment in water for 1 h at 80 °C, in a 0.03% sodium carbonate solution for 3 h at 80 °C, again in water for 1 h at 80 °C, and finally washed with cold water until neutrality was obtained and dried in a vacuum oven at 105 °C for analysis (Gismatulina et al., 2016a). The mass fraction of nitrogen in the synthesized nano-nitrocellulose samples was determined by the Kjeldahl nitrogen determination method, and the yields of NNC samples were calculated using the following equation:

$$\text{Yield}\,(\%) = \frac{W_p}{W_o} \times 100 \tag{3.7}$$

Where W_p and W_o are the weights (g) of the synthesized NNC sample and nanocellulose sample used for nitration, respectively. Generally, the overall steps performed to synthesize

nanonitrocellulose from water hyacinth and the results obtained at each step were summarized by the flow diagram as shown in Figure 3.2.

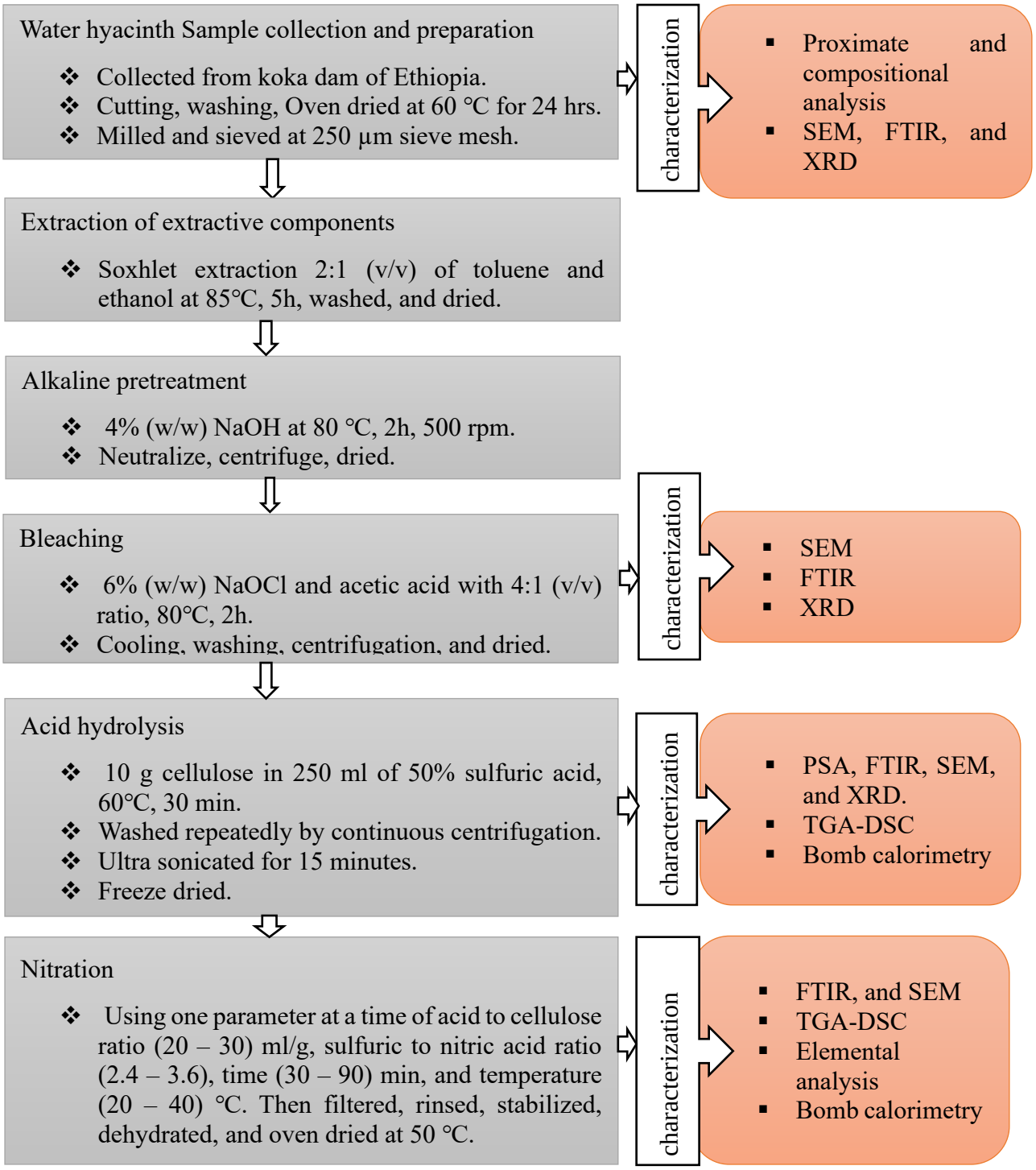


Figure 3.1: The general scheme for the isolation of cellulose, nanocellulose, and nanonitrocellulose synthesis from water hyacinth.

Figure 3.2: Flow diagram for the synthesis of nanonitrocellulose from water hyacinth

3.3. Experimental Design

After nanocellulose was extracted from water hyacinth, the effects of nitration conditions on the yield of nano nitrocellulose in terms of the desired degree of substitution were investigated by using one factor at a time experimental design at nitrating acid mixture to nanocellulose ratio (esterification coefficient) (20:1–40:1) ml/g, sulfuric acid to nitric acid ratio (2.4–3.6), nitration time (20–60) min, and nitration temperature (20–40) °C. These process variables and conditions were chosen from the esterification of oat-hull cellulose (Korchagina & Budaeva, 2019).

Table 3.1: One factor at a time experimental design for four parameters at five levels of each.

Run	Esterification coefficient (ml/g)	Sulfuric acid to nitric acid ratio	Time (min)	Temperature (°C)	Desired degree of substitution (DS)
1	20	3.0	40	30	-
2	25	3.0	40	30	-
3	30	3.0	40	30	-
4	35	3.0	40	30	-
5	40	3.0	40	30	-
6	30	2.4	40	30	-
7	30	2.7	40	30	-
8	30	3.0	40	30	-
9	30	3.3	40	30	-
10	30	3.6	40	30	-
11	30	3.0	20	30	-
12	30	3.0	30	30	-
13	30	3.0	40	30	-
14	30	3.0	50	30	-
15	30	3.0	60	30	-
16	30	3.0	40	20	-
17	30	3.0	40	25	-
18	30	3.0	40	30	-
19	30	3.0	40	35	-
20	30	3.0	40	40	-

3.4. Characterization

3.4.1. Fourier Transform Infrared Radiation (FTIR)

A Fourier transform infrared spectrometer (FTIR) was used to study the changes in functional groups present in the materials before and after their production process. Raw water hyacinth, bleached cellulose, synthesized nanocellulose, and its nitrated derivative nanonitrocellulose samples were scanned using the FTIR spectrometer in attenuated total reflectance (ATR) mode, and the spectra were recorded over a range of 4000–400 cm^{-1} wave number in transmittance mode by making the sample in powder form and mixing it with KBr powder.

3.4.2. Scanning Electron Microscopy (SEM)

Morphological changes of raw water hyacinth before and after treatment are demonstrated by using scanning electron microscopy (JCM-6000PLUS Bench Top SEM, JEOL, Japan) at Adama Science and Technology University (ASTU), Ethiopia, with an accelerating voltage of 5.0 kV. Hence, SEM was used to observe the morphological surface of raw water hyacinth, bleached cellulose, extracted nanocellulose, and nitrated nanocellulose.

3.4.3. Particle Size Analyzer (PSA)

The particle size of the synthesized nanocellulose was determined by using the Malvern Zetasizer Nano instrument (ZE3600) at Addis Ababa Science and Technology University. The nano-cellulose sample was analyzed within the range of 0.1 nm to 10 μm under the following conditions of water refractive index of 1.330, viscosity of 0.8872 cp, and temperature of 25 ℃.

3.4.4. X-Ray Diffraction (XRD)

The crystal forms and crystallinity of raw water hyacinth, bleached cellulose, and nanocellulose were characterized by X-ray diffractometer (XRD). The change in crystallinity index and average crystallite size of the samples from raw WH to nano-crystalline cellulose (NCC) were evaluated by X-ray diffraction patterns. The powder of raw WH, bleached cellulose, and nanocellulose samples were scanned at room temperature with a diffraction angle in the range of 5° to 80° and a step size of 0. 02°.The index of crystallinity (CrI) and average crystallite size (D) of the samples were computed by using the Scherrer equation as in equation numbers 3.8 and 3.9 below, respectively.

$$CrI\,(\%) = \frac{\sum A_{crs}}{\sum A_{crs} + \sum A_{amr}} \times 100 \tag{3.8}$$

$$\mathrm{D(nm)} = \frac{k\lambda}{\beta \cos\theta} \tag{3.9}$$

Where CrI is the crystallinity index, A_{crs} is the peak area for the crystalline part, A_{amr} is the peak area for the amorphous part, D is the average crystallite size, k is the form factor or Scherrer constant (0.9), β is the full width half maximum (FWHM) of maximum intensity in radians, λ is the wave length of the x-ray source (0.154 nm), and θ is the diffraction angle of the peak in radians.

3.4.5. Thermal Analysis (TGA-DSC)

The thermal study is a key criterion used to investigate the thermal behavior and evaluate the potential of energetic compounds for real-world applications. Hence, TGA analysis was performed to see the thermal behavior of raw precursor nanocellulose and synthesized nano-nitrocellulose samples by using a TGA-DSC thermogravimetric analyzer. Runs were performed by weighing out a 10 mg sample in a platinum pan. The analysis was performed in a temperature range of 20 to 700 °C under a constant flow rate of 50 mL/min of nitrogen and 20 °C/min of heating rate. Finally, the weight loss or heat evolved was measured against increasing temperature.

3.4.6. Elemental Analysis

One of the most important factors that affects the properties and applications of nitrocellulose is the degree of nitration, which is the amount of nitrogen content available in the final product. So, the Kjeldahl nitrogen determination method was used to determine nitrogen content at the Leather Industry Development Institute (LIDI), Addis Ababa, Ethiopia. The nano-nitrocellulose samples of 1.5 grams each were weighed and digested with concentrated sulfuric acid in the digestion unit under the condition of a copper sulfate catalyst to aid the digestion process until the sample started to decompose and release nitrogen-containing compounds. After digestion, those nitrogen-containing compounds were converted into ammonia under an alkaline condition in the presence of NaOH, which is distilled out with steam and absorbed by excess boric acid solution. Then, after titration with a standard solution of hydrochloric acid, calculate the nitrogen content of the sample.

3.4.7. Energetic performance evaluation

The determinations of calorific values of nanocrystalline nitrocellulose and its precursor were made using an adiabatic bomb calorimeter (model 6100 series, manufactured by Parr Instrument Company) in the Geological Institute of Ethiopia, Addis Ababa, Ethiopia, by weighing 2 g of each sample into an ignition cup, then wrapping it with a fuse wire and sealing it inside the bomb. The bomb was then filled with 30 atmospheres of oxygen and placed in a static jacket filled with 2 liters of water. After combustion has taken place for about 6 minutes, the calorific value was read out on the screen of the calorimeter in Cal/g. A differential scanning calorimeter (DSC) thermogravimetric analyzer was also used to determine the amount of energy released after complete burning (heat of decomposition) of the samples, which evaluated the energetic properties of the samples.

Moreover, by using the liquid immersion technique and water as the displacement liquid, the pycnometer method was used to quantify the density of each sample, as illustrated by (Adeleye et al., 2019). The pycnometer bottle (50 ml) was weighed empty with the stopper (W). It was filled with water to the brim, and the excess was wiped off with absorbent paper and the weight with the stopper was noted as (W_1). The difference between W and W_1 was recorded as W_2. Two grams of each sample were weighed (W_3), transferred into the pycnometer bottle, and filled with water to the brim. The excess solvent was wiped off and the bottle weighed again with the stopper (W_4). The density (g/cm^3) was then calculated using equation (3.10):

$$Density\ (g/cm^3) = \frac{W_2 \times W_3}{50\ (W_3 - W_4 + W + W_2)} \tag{3.10}$$

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Proximate Analysis of Water Hyacinth

The proximate analysis provides information about the biomass in terms of volatile matter, ash content, fixed carbon, and moisture content. It helps to determine the potential of biomass for various applications such as energy production, animal feed, and soil amendment. Volatile matter refers to the condensable and non-condensable gases that are released from the biomass when it is heated. The amount depends on the heating rate and final temperature. Most lignocellulosic biomass has a high volatile matter content (up to 80 percent) (Jimoh et al., 2016). Ash is the solid residue left after the complete combustion of the biomass. Fixed carbon indicates the percentage of biomass burned in the solid state after the expulsion of the volatile matter, while moisture is the amount of water present in the biomass. The result of the proximate analysis for water hyacinth was presented in Table 4.1, which confirms the literature values as cited as references in the same table.

Table 4.1: Results for proximate analysis

Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon (%)	Reference
4.21 ± 0.16	58.42 ± 0.18	18.84 ± 0.25	18.53 ± 0.31	This work
3.48 ± 0.26	57.67 ± 2.28	19.80 ±1.25	22.53 ± 2.33	(Jimoh et al., 2016)
4.9	61.2	20.1	13.8	(Sukarni et al., 2019)
9.95	56.30	16.35	17.40	(L. Huang et al., 2017)

4.2. Compositional analysis

Before going to the application, it is very important to analyze the composition of lignocellulosic biomass in order to understand the suitability of the biomass for the targeted purpose. This means it is vital to recognize the components of water hyacinth before the extraction of cellulose since the cellulose, hemicellulose, and lignin content of water hyacinth feedstock played an awesome role in the final yield of the product. The main chemical composition of lignocellulosic biomasses

consists of cellulose, hemicellulose, and lignin, and the content of these components depends on biomass type, species, growing condition, and method for determination (Abdul Khalil et al., 2016). In this work, the cellulose, hemicellulose, and lignin contents of raw water hyacinth were 34.04, 27.64, and 15.7, respectively, which were well comparable with those of water hyacinth fibers available in the literature, especially those presented in Table 4.2. But this small deviation may be due to geographical location, methods used for analysis, and the different types and concentrations of solvents used.

Table 4.2: Results for Compositional analysis

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
34.04 ± 0.32	27.64 ± 0.12	15.7 ± 0.24	This work
46.15	13.46	23.07	(Fitrya et al., 2021)
43.01	29.13	6.9	(Id et al., 2018)
28.23	26.35	17.44	(Cheng et al., 2010)
55	19	14	(Ewnetu Sahlie et al., 2022)

4.3. Isolation of Cellulose from Water Hyacinth

Cellulose was extracted from the water hyacinth stem by following various physiochemical treatment processes, including Soxhlet extraction, alkaline treatment, and bleaching. Soxhlet extraction was used to remove extractive components such as lipids, waxes, alkaloids, proteins, simple and complex polyphenols, simple sugars, pectins, starch, essential oils, and other organic soluble ingredients (Packiam et al., 2021). To achieve this, a 2:1 (v/v) combination of toluene and ethanol was utilized as the solvent. After Soxhlet extraction, a strong base, NaOH, was used in the alkalization process, which removed the lignin and hemicellulose components from the water hyacinth cellulose. Then, a mixture of 6% sodium hypochlorite solution and acetic acid at a ratio of 4:1 (v/v) was used in the bleaching process for the alkali-treated samples. There will be a small amount of lignin and hemicellulose left in the alkali-treated sample, which this mixture of sodium hypochlorite and acetic acid can eliminate (Sundari & Ramesh, 2012). The greenish-yellow fiber changes to white during this process.


a)


b)

Figure 4.1: a) Bleached water hyacinth cellulose; b) CNC suspension

The removal of the hemicellulose and lignin is indicated by the change in color of the white. Then the green color of the water hyacinth powders diminished and turned to pure white after each of the above pretreatment steps, as shown in figure 4.1a.

4.4. Preparation of Nanocellulose from the Isolated Cellulose

After bleaching, the purified cellulose fibers were subjected to sulfuric acid hydrolysis, which isolated CNCs that showed high stability in water. The hydrolysis process was carried out at optimized and controlled conditions of 50% sulfuric acid at 60°C for 30 minutes and continuous agitation at 500 rpm (Pantamanatsopa, Ariyawiriyanan, Ekgasit, et al., 2023). Due to the combinations of ordered and disordered regions in cellulose chains, the disordered regions can be hydrolyzed by acid, and the ordered one is left as the remaining one (Lavoine et al., 2012). After hydrolysis, various steps such as sequential centrifugation, neutralization to remove free sulfate, ultrasonication, and freeze-drying were performed to obtain purified cellulose nanocrystals. The strong acid helps to break bonds in the cellulose and convert it into microcrystalline cellulose. The ultrasonication process carried out also facilitates the breakdown of microcrystalline cellulose into nanocrystalline ones (Khalil et al., 2014). The β-(1-4)-glycosidic bonds of cellulose were broken during ultrasonic treatment. The obtained suspension of cellulose nanocrystal was shown in Figure 4.1b, and the yield of the obtained cellulose nanocrystal based on bleached cellulose was 34.6%, which is comparable with the previous studies that attempted to isolate cellulose nanocrystal under varying experimental conditions, obtaining yields between 30 and 34%, as reported by (Oyeoka et al., 2021). This much reduced yield may be due to different external factors, such as a loss during washing and centrifugation treatments, which play a role in the weight loss of nanocellulose.

4.5. Preparation of nanonitrocellulose

The preparation of nanonitrocellulose involves the nitration of nanocellulose using a mixture of concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4) with the desired ratios. Nitric acid is a source of nitro groups ($-NO_2$) used for substitution of the hydroxyl groups (-OH) available in the cellulose chains during the nitration process. But the sulfuric acid acts as a catalyst and dehydrating agent, facilitating the nitration reaction.

The chemical composition of raw water hyacinth used to isolate nanocellulose and synthesize nanonitrocellulose was as follows: the weight fraction of cellulose was 34.04%, the weight fraction of lignin was 15.7%, and the weight fraction of ash content was 18.84%. This raw material was used to synthesize nanocellulose by using a series of dewaxing, alkalization, bleaching, acid hydrolysis, and ultrasonication methods. A detailed description of the preparation conditions is provided in Figure 3.3. Then, after using the above methods, a uniform, rod-like shape or whisker shape of nanocellulose was isolated from water hyacinth and obtained the following characteristics: 93.2% weight fraction of cellulose and 0.12% weight fraction of acid-insoluble lignin. This result is comparable with many previous studies that used these lignocellulosic biomass pretreatment methods for removing non-cellulosic materials.

For instance, (Johar et al., 2012) pretreated rice husks with alkaline followed by a bleaching process and found an increased cellulose content from 35% in untreated rice husks to 96% by weight in products after alkaline and bleaching pretreatments. In a similar way and for the same purpose (Budaeva & Gismatulina, 2018), they also isolated cellulose with weight fractions of 94.3%, 90.7%, and 87.8% from oat hulls, miscanthus, and intermediate flax straw, respectively. This indicates that the purification steps that were used to isolate nanocellulose effectively removed impurities and non-cellulosic components. The high cellulose content obtained ensures that a significant portion of the nanocellulose can be nitrated, leading to higher degree of substitution and the desired properties of nanonitrocellulose. Table 4.3 shows the basic characteristics of synthesized nanonitrocellulose samples.

Table 4.3: Basic characteristics of synthesized NCNC samples

Runs	Nitrogen content (%)	Yield (%)	Degree of substitution (DOS)
$A_{20}B_{3.0}C_{40}D_{30}$	12.20	130	2.32
$A_{25}B_{3.0}C_{40}D_{30}$	12.58	134	2.44
$A_{30}B_{3.0}C_{40}D_{30}$	12.85	137	2.53
$A_{35}B_{3.0}C_{40}D_{30}$	12.83	134	2.525
$A_{40}B_{3.0}C_{40}D_{30}$	12.82	134	2.521
$A_{30}B_{2.4}C_{40}D_{30}$	11.54	133	2.12
$A_{30}B_{2.7}C_{40}D_{30}$	12.60	134	2.45
$A_{30}B_{3.0}C_{40}D_{30}$	12.99	143	2.58
$A_{30}B_{3.3}C_{40}D_{30}$	12.85	135	2.53
$A_{30}B_{3.6}C_{40}D_{30}$	12.45	130	2.4
$A_{30}B_{3.0}C_{20}D_{30}$	10.57	128	1.85
$A_{30}B_{3.0}C_{30}D_{30}$	12.34	131	2.38
$A_{30}B_{3.0}C_{40}D_{30}$	12.97	141	2.57
$A_{30}B_{3.0}C_{50}D_{30}$	12.97	140	2.57
$A_{30}B_{3.0}C_{60}D_{30}$	12.79	135	2.51
$A_{30}B_{3.0}C_{40}D_{20}$	12.76	134	2.50
$A_{30}B_{3.0}C_{40}D_{25}$	12.82	134	2.52
$A_{30}B_{3.0}C_{40}D_{30}$	12.90	138	2.57
$A_{30}B_{3.0}C_{40}D_{35}$	12.91	139	2.55
$A_{30}B_{3.0}C_{40}D_{40}$	12.88	136	2.54

Where A = esterification coefficient, B = sulfuric to nitric acid ratio, C = nitration time, D = nitration temperature, and the subscripts indicate the respective quantity.

It is worth nothing that high quality nanonitrocellulose is produced using nanocellulose precursors containing not less than 92% cellulose and a maximum of 1.2% non-cellulose component content (Gismatulina et al., 2016). The synthesized NNC samples in this study had the following quality, as shown in Table 4.3: nitrogen content of 10.57-12.99% and **t**he yield of NNC was ranged from 128-144% which is greater than 100% because the average molecular weight was increased after

nitration by the substitution of nitro groups for hydrogen atoms in cellulose hydroxyls (J. Liu, 2019).

4.6. Characterization

4.6.1. Fourier Transform Infrared Radiation (FTIR) Analysis

Lignocellulosic biomasses primarily consist of amorphous lignin, hemicellulose, and crystalline cellulose, and these components can be characterized by looking at their functional groups in the FTIR analysis (Wulandari et al., 2016). The spectrum of raw water hyacinth, bleached cellulose, cellulose nanocrystal, and nitrated cellulose nanocrystal was carried out in the FTIR characterization and shown Figure 4.2.

In the wave number range of 3400-3300 cm^{-1}, 3000-2800 cm^{-1}, 1750-1500 cm^{-1}, and 1100-1000 cm^{-1} four major peaks were observed in the spectrum of raw water hyacinth, bleached cellulose, and cellulose nanocrystal. As a result of hydrogen bond interaction with hydroxyl groups, the stretching of OH is represented by the characteristic peaks in all samples within the range of 3400 – 3300 cm^{-1} (Asrofi et al., 2017). In all samples, the spectra linked to C-H stretching were observed at wave numbers 3000-2800 cm^{-1}. Therefore, all samples have aliphatic saturated components, as indicated by this C – H cluster (Lani et al., 2014). Due to the presence of C=O bonds, which indicate the presence of lignin and hemicellulose, the untreated raw water hyacinth exhibited an intense and sharp peak at the 1610 cm^{-1} (Abraham et al., 2011). This peak tends to decrease following chemical and mechanical treatments. Lignin's aromatic ring vibration appeared to happen between 1500 and 1200 cm^{-1} (Mora, 2008). This distinctive peak, which was present at around 1200-1300 cm^{-1} in the untreated raw water hyacinth but not in the treated samples, shows that the lignin component was effectively eliminated after chemical and mechanical treatments, and increasing the cellulose component. The analysis of chemical composition confirmed this result as well. The characteristic peak caused by the stretching of the pyranose ring's C-O-C in cellulose can be found in the range of wavenumber 1000 – 1030 cm^{-1} (Thi et al., 2022). In the three samples, this peak was present, as shown in the figure 4.2.

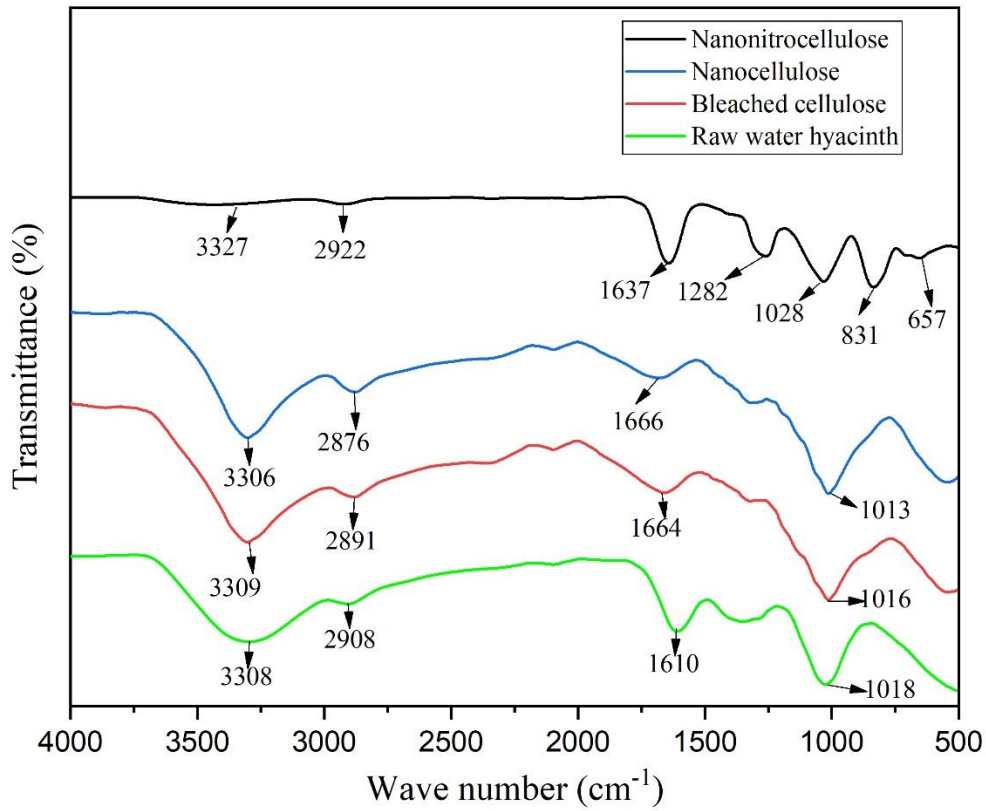


Figure 4.2: FTIR spectra of raw water hyacinth, bleached cellulose, nanocellulose, and nitrocellulose nanocrystal

According to the comparison of the FTIR spectra of water hyacinth nanocellulose and nanonitrocellulose in Figure 4.2, the stretching peak of the hydroxyl groups of the synthesized nanonitrocellulose (DS = 2.58) near the wave number of 3327 cm^{-1} was significantly reduced. This indicates that the hydroxyl groups were substituted by the nitro groups. Following nitration, the spectrum distinctly displays the usual signal pattern that was observed in the nitrocellulose sample (Trache, 2016). As shown in Figure 4.2, the right half of the spectrum is composed of five distinct peaks: two distinct intense peaks at approximately 1637 and 1282 cm^{-1}, which correspond to the asymmetric and symmetric stretching of NO_2; a slightly broad intense peak at approximately 1028 cm^{-1}, which is assigned to the ONO_2 stretching; a less intense peak at 831 cm^{-1}, corresponds to the asymmetric bending of ONO_2, and a band at approximately 657 cm^{-1}, which is assigned to ONO_2 bending. Similar results were reported in the previous studies (Maklakova & Gustova, 1994; Gismatulina et al., 2018). Overall, all of the nitro group representative peaks are visible in the water hyacinth based nanonitrocellulose FTIR spectrum.

4.6.2. Scanning electron microscopy (SEM) analysis

SEM analysis provides valuable visual information about the changes observed in the morphology and surface structure of raw water hyacinth, bleached cellulose, the extracted nanocellulose, and nitrated nanocellulose throughout the process, as shown in Figure 4.3. It is clearly shown that, the untreated (raw water hyacinth) in Figure 4.3(a) is evidently made up of microfibrils which are firmly connected by a mass of adhesive substances, most likely waxes, and oils, which also give the raw water hyacinth sample a smooth appearance (Abraham et al., 2011; Julie Chandra et al., 2016). The morphology of the sample of bleached water hyacinth is displayed in Figure 4.3(b). The pale appearance of the surface indicates the removal of non-cellulosic materials like lignin, hemicellulose, wax, and oil (Mathew et al., 2010).

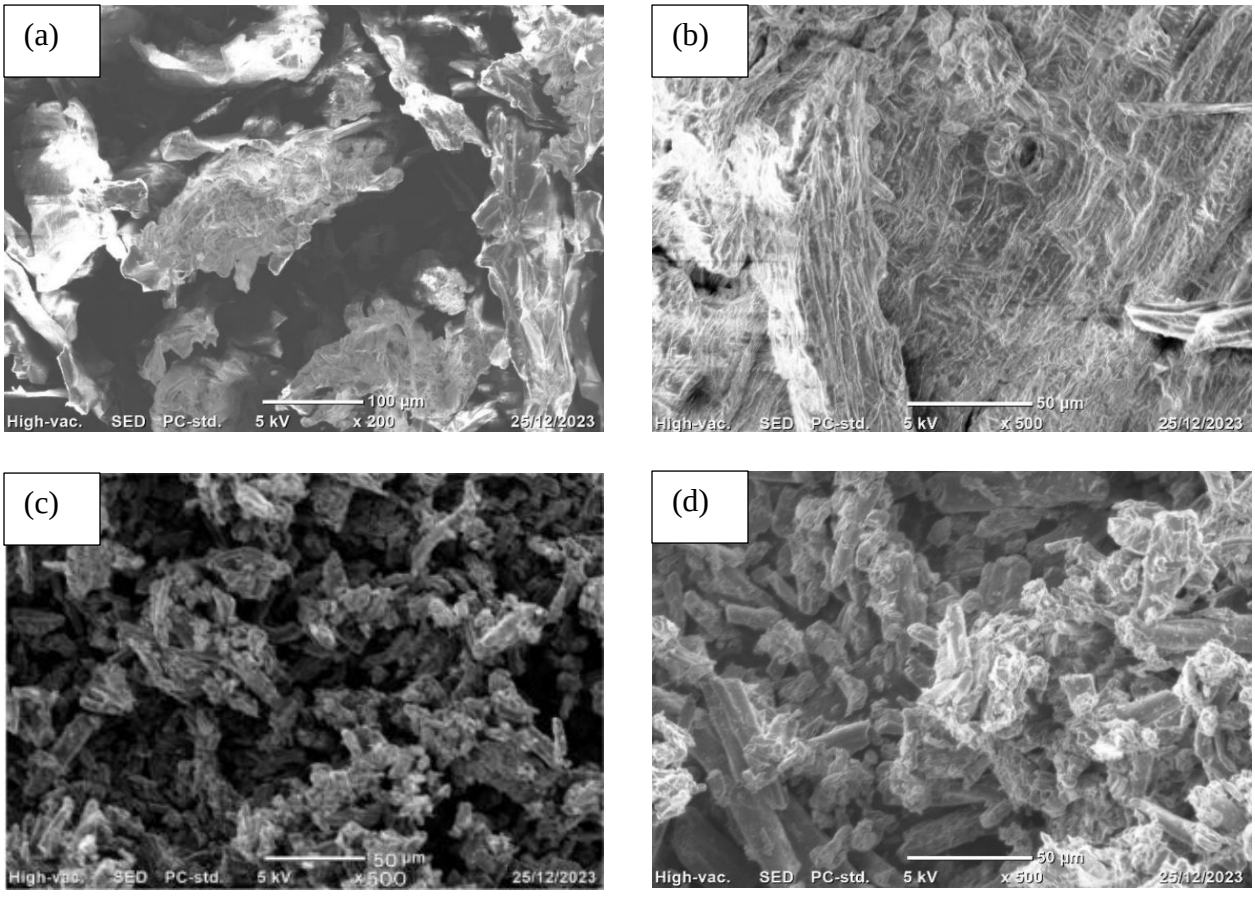


Figure 4.3: SEM images of (a) raw water hyacinth, (b) bleached cellulose, (c) cellulose nanocrystal, and (d) nitrated nanocellulose

Following bleaching, acid hydrolysis and sonication were used to treat the sample. As a result, the fiber's size decreases, and the fiber appears to be made up of individual microfibrils, as shown in

the Figure 4.3(c). Depolymerization is the cause of this outcome, which has been noted in earlier research (Abraham et al., 2011; Mora, 2008; Abraham et al., 2013; Lee et al., 2014).

The initial nanocellulose (Figure 4.3 (c)) is clearly a whisker-shaped structure made up of interlaced fibers. The nitrated nanocellulose structure (Figure 4.3(d)) became more compact and denser after it was nitrated, indicating that the pure nanocellulose had undergone modification following nitration. In accordance with the findings of the other study (Trache et al., 2014; Okada et al., 2021; Gismatulina & Budaeva, 2017), the nitration partially reorganized the Microfibrils and maintained the original nanocellulose's structure after nitration, just with a larger fiber volume.

4.6.3. Particle Size Analysis

The particle size distribution and average particle size of the synthesized nanocellulose suspension were determined by using the dynamic light scattering technique. As shown in figure 4.4, it can be observed that the majority of particles had dimensions in the nanoscale range, with an average effective diameter of 91.3 nm and a particle size distribution of 58.77 nm to 220.20 nm. Therefore, it is clear that nanocellulose was successfully extracted on a nanoscale through the sulfuric acid hydrolysis of cellulose.

Table 4.4: Size comparison of nanocellulose obtained from previous studies from different sources

Source	Extraction method	Size (nm)	Reference
Cotton linter	Acid hydrolysis	9.2	(Paulo et al., 2013)
Enset fiber	Acid hydrolysis with sonication	66	(Beyan et al., 2021)
Olive fiber	Alkaline treatment	168	(Kian et al., 2020)
Water hyacinth	Alkaline treatment, bleaching, acid treatment, and sonication	15.61	(Asrofi et al., 2017)
Water hyacinth	Alkalization, bleaching, acid hydrolysis, and sonication	93.02	(Packiam et al., 2021)
Waste cotton	Enzymatic hydrolysis and sonication	70	(Meyabadi et al., 2014)
Eragrostis teff straw	Acid-chlorite delignification, alkali, and acid hydrolysis	100	(Bacha, 2022)
Water hyacinth	Alkaline pretreatment, bleaching, and acid hydrolysis	91.3	This work

The other information that was given by the instrument is the polydispersity index (PDI), which describes the uniformity of the sample. If the PDI value is higher, the uniformity of the sample is lower. The PDI scale ranges from 0 to 1 (with typically 0.3 to 0.7 being nearly monodisperse and for PDI > 0.7 being polydisperse) (Stetefeld et al., 2016). In this study, the PDI value was obtained as 0.327, which confirms good uniformity of the synthesized nanocellulose.

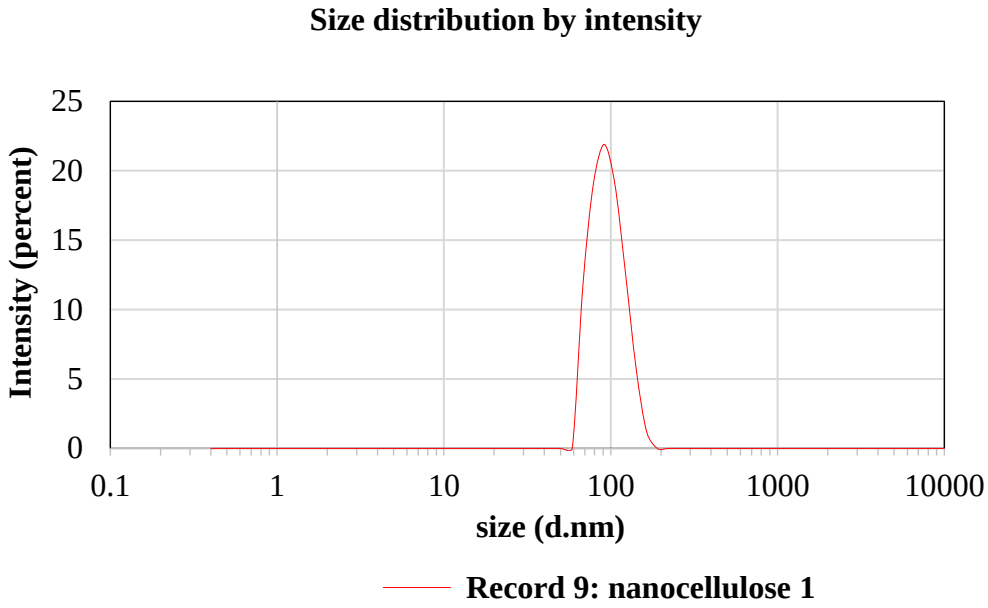


Figure 4.4: Particle size distribution of nanocellulose obtained by dynamic light scattering (DLS)

4.6.4. X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis is a widely used technique for studying the crystallographic properties of materials, including phase identification, crystallinity analysis, crystal size, and amorphous content analysis. The XRD intensity curve of raw water hyacinth, water hyacinth cellulose, and CNCs is demonstrated in figure 4.5. The XRD pattern of raw water hyacinth, water hyacinth cellulose, and CNCs revealed significant peaks around 2θ of 15.3, 22.8, and 34.6 related to its crystalline structure, cellulose (Pakutsah & Aht-ong, 2020). The XRD profiles for all three samples are similar except for a small shift in peak position, indicating that all samples contain cellulose.

The crystalline index and crystalline size showed a positive correlation, as shown in Table 4.5. In addition, the raw water hyacinth fiber crystallite size increased from 0.041 to 0.183–0.194 for

WHC–CNCs. In fact, alkalization, bleaching, and acid hydrolysis improved the crystalline size of cellulose following the removal of its amorphous domains (Jonoobi et al., 2009). That is, alkalization and bleaching eliminated lignin and hemicellulose and realigned the domains of the crystal. Following alkalization and bleaching, the residual randomly oriented amorphous was removed by acid hydrolysis with ease because the hydronium ions were able to effectively enter amorphous domains, leading to the hydrolytic cleavage of cellulose glycosidic bonds and larger crystal sizes (Pantamanatsopa, Ariyawiriyanan, & Ekgasit, 2023).

Between the three samples, there is a significant variation in peak intensity that represents variations in the crystallinity index. In comparison to water hyacinth cellulose and cellulose nanocrystal, the raw water hyacinth crystallinity index (22) was significantly smaller, as shown in Table 4.5. This effect is caused by acid hydrolysis, bleaching, and the elimination of lignin and hemicellulose components in alkaline treatment (Julie Chandra et al., 2016).

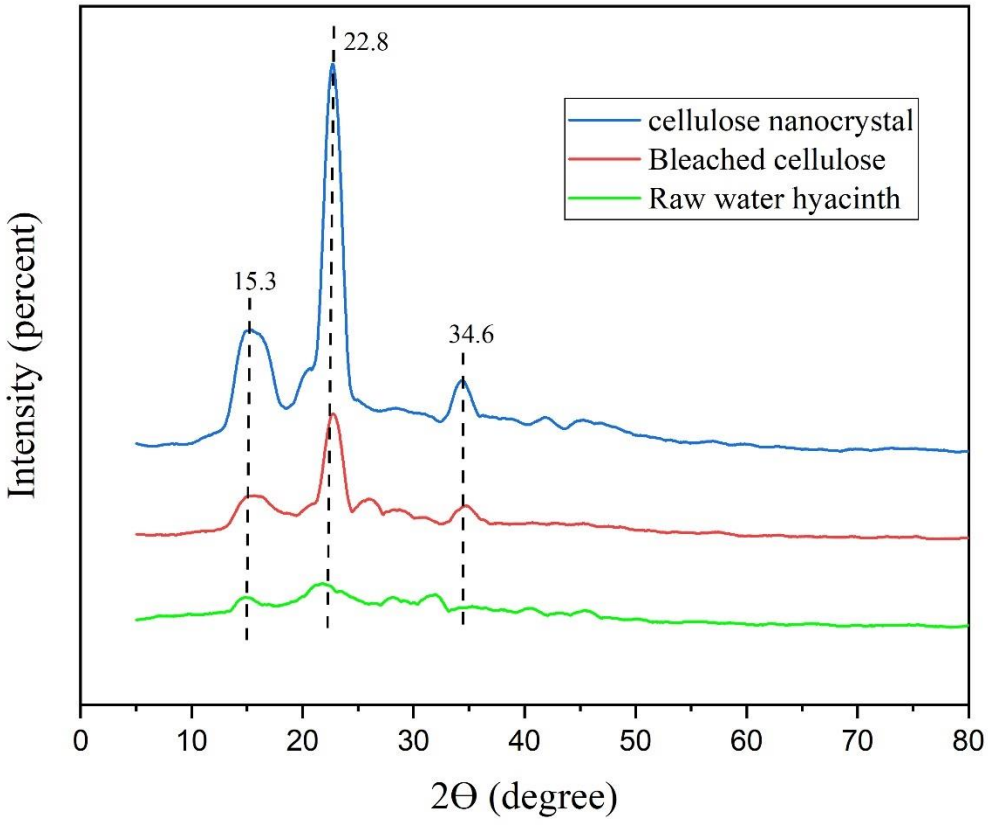


Figure 4.5: XRD pattern of samples after different treatment steps

This study indicated that the extraction process had the potential to isolate cellulose and, in turn, nanocellulose from the raw water hyacinth**.** Similar findings were reported by several researchers who worked with nanocellulose synthesis from lignocellulosic biomasses (Chaiwarit et al., 2022; Julie Chandra et al., 2016; Wulandari et al., 2016).

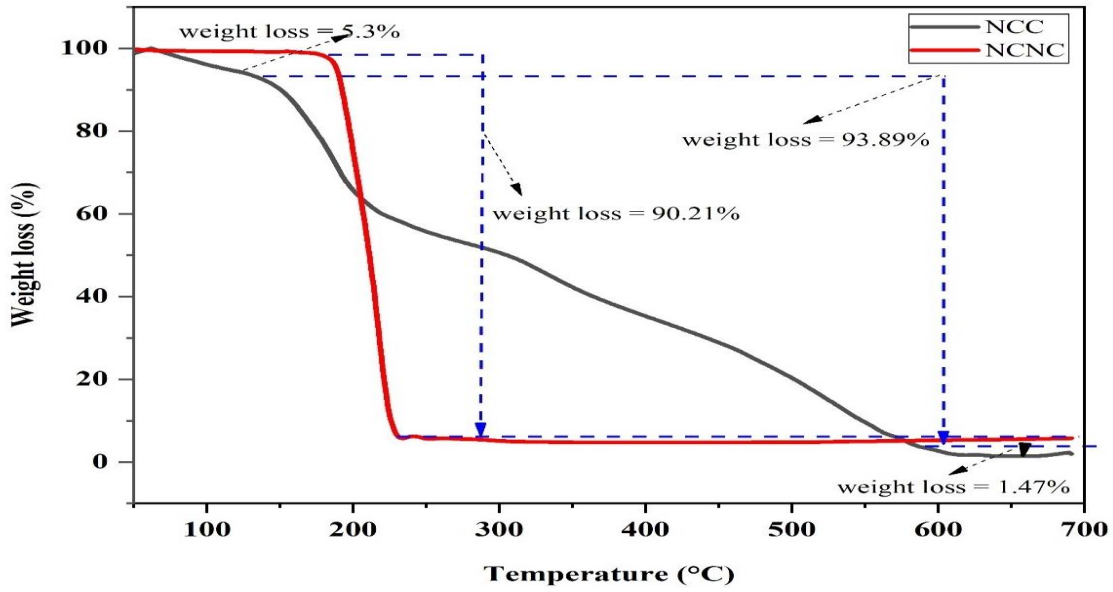
Table 4.5: Crystallinity index and average crystallite size at various treatments

Samples	Index of crystallinity (%)	Average crystallite size (nm)
Raw water hyacinth	22	0.041
Bleached cellulose	54	0.183
Cellulose nanocrystal	76	0.194

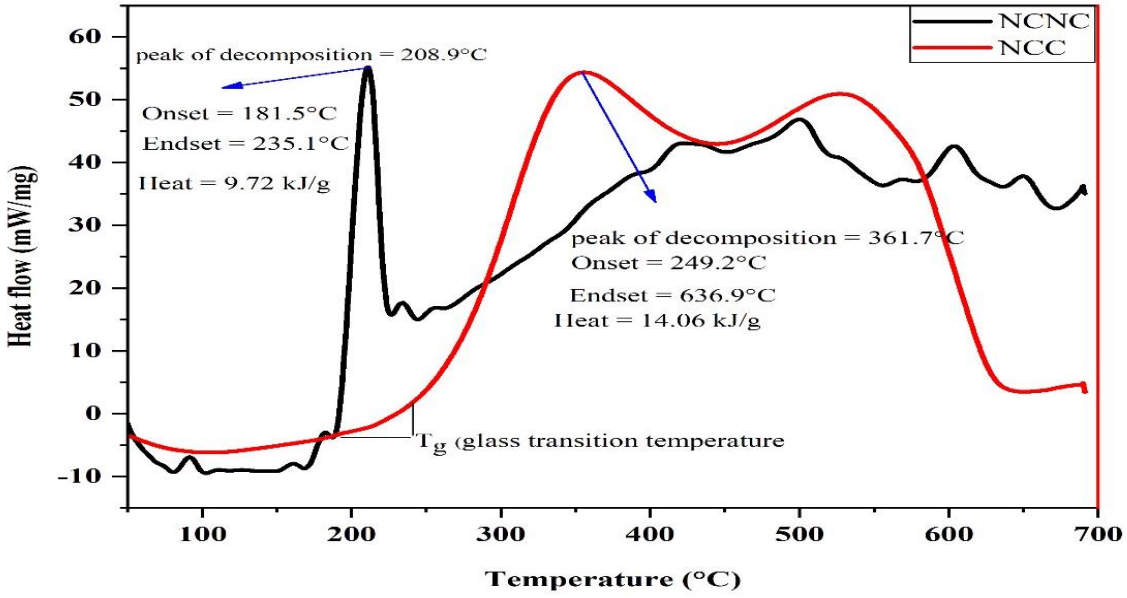
4.6.5. Thermal analysis (TGA - DSC)

Thermal performance is mostly regarded as a fundamental parameter for energetic materials (Benhammada & Trache, 2020). In order to use nitrated nanocellulose as an ingredient of propellant formulation, its property is directly linked to its thermal decomposition temperature, which leads to a sufficient quantity of gas. Therefore, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for nanocellulose and nitrated nanocellulose were performed and are shown in Figure 4.6. The nanocellulose sample experimental curve for the thermogravimetric analysis (TGA) as shown in figure 4.6a displayed three distinct TGA regions: the first occurred when the sample is dried out to show a 5.3% weight loss starting from the test up to 111.4°C; the second occurred when the sample was heated to 610°C and decomposed with a 93.89% weight loss; and the third occurred when the sample was heated up to 680°C and continued to decompose with a minor 1.47% weight loss. It is well known that thermal stability increases with a higher purity cellulose sample and a higher decomposition onset temperature (Pacheco et al., 2017). The collected information in this study of thermal analysis is consistent with the results of the study carried out in (Skiba et al., 2023; Wulandari et al., 2016; Ridara et al., 2020; Sultana et al., 2020). The thermal gravimetric analysis (TGA) findings for the NCNC sample (Figure 4.6a) show that the main thermal degradation of the NCNC sample begins at 181.5–235.1 °C with a peak temperature of 208.9 °C and continues until 310.3 °C, during which the sample weight changes by 90.21%. That was the case for the TGA curve, which exhibited a single sharp exothermic behavior with a maximum peak of 208.9◦C, accompanied by a sharp weight loss.

Subsequently, the NCNC sample exhibits continued degradation, resulting in a weight loss of 1.01%. The thermal degradation of nitrocellulose, whatever size it is, for propellant formulation falls in the range of 190–210 °C (Sovizi et al., 2009b; Pourmortazavi et al., 2009; Huang et al., 2023) and the synthesized nano nitrocellulose showed similar thermal behavior with these of previous studies.



(a)



(**b**)

Figure 4.6: TGA – DSC curves of nanocellulose and nitrated nanocellulose (a) (TGA) (b) (DSC)

Figure 4.6b depicts the DSC curve of the NCC and NCNC samples, which showed a decomposition peak at 361.7◦C and 208.9◦C, respectively. As shown from the DSC analysis of nanocrystalline cellulose (NCC) (Figure 6b), an initial broad endothermic band from 40 °C to 140 °C was observed, where heat energy was absorbed to volatize the water molecules (Fouad et al., 2020). The other more intense second transition peak in the region below 450 °C occurred as a result of the melting of the cellulose component in the sample (Rashid & Dutta, 2020). It is also observed that NCC has a glass transition point at around 200-250°C (Fahma et al., 2021).

As shown in the DSC curve of NCNC, a significant change of heat flow and mass was not observed at temperature ranging from 100 ºC to 170 ºC, which indicated slow decomposition took place at these temperatures as described by previous studies (Luo et al., 2018). The DSC curve of the synthesized NCNC sample (Figure 4.6b) showed a single, narrow exothermic peak at 190.34–208.9 ◦C along with a drop in NCNC sample weight to 90%, indicating a high level of chemical purity. The information on cellulose nitrates from microcrystalline cellulose (Tarchoun et al., 2021), commercial cotton cellulose (Trache, 2016), and NBC (Cellulose, 2023) is comparable to the results obtained, but it can be concluded that thermal stability decreases with increasing nitrogen content . When comparing the DSC curve of the NCNC sample and the original NCC, it is evident that the peak temperature of the nitrated cellulose drops from 361.7◦C to 208.9◦C and decomposed in one step. This is due to the fact that cellulose with a high nitrogen content has more nitrate ester and cellulose with a low nitrogen content has more hydroxyl groups (-OH). When it comes to thermal degradation, $-NO_2$ breaks down more quickly than (-OH) (Lin et al., 2010). The enhanced thermal degradation of the polymeric cellulose chains can be attributed to the homolytic cleavage of the thermally instable $O-NO_2$ bonds.

The synthesized NCNC sample had high specific heats of decomposition (9.72 kJ/g), which is in agreement with its calorific value (10.04 KJ/g) as determined by a bomb calorimeter and validates its energetic property. This energy value is sufficient to produce pressure for propellant application and this result is comparatively similar to other studies (Lemieux & Prud'Homme, 1985; J. Liu & Chen, 2018; Korchagina, et al., 2019).

4.6.6. Elemental Analysis

Elemental analysis of the synthesized nanonitrocellulose samples was performed using the Kjeldahl method to determine nitrogen content, and consequently, the degree of substitution of

each sample was calculated using equation (2.1). The values of nitrogen content, degree of substitution, and yield of the prepared nano-nitrocellulose samples are shown in Table 4.3. In this study, the effect of nitration conditions (acid mixture to nanocellulose ratio, sulfuric acid to nitric acid ratio, time, and temperature) on the degree of substitution of the synthesized nanonitrocellulose was discussed as follows:

4.6.6.1. Effect of acid mixture to nanocellulose ratio on DS of nanonitrocellulose

Since the nitration reaction is an incomplete, reversible, and heterogeneous chemical reaction, the key factor determining the degree of substitution of the nitrated product is not entirely at the beginning of the reaction but in the final acid composition. Therefore, the effect of the esterification coefficient on degree of substitution (DS) was investigated, and the results are shown in figure 4.7. In this experiment, the ratio of sulfuric acid to nitric acid, nitration time, and nitration temperature were fixed at 3, 40 min, and 30 °C, respectively, with the esterification coefficient changing from 20 to 40 ml/g by an increment of five, as shown in Table 3.1.

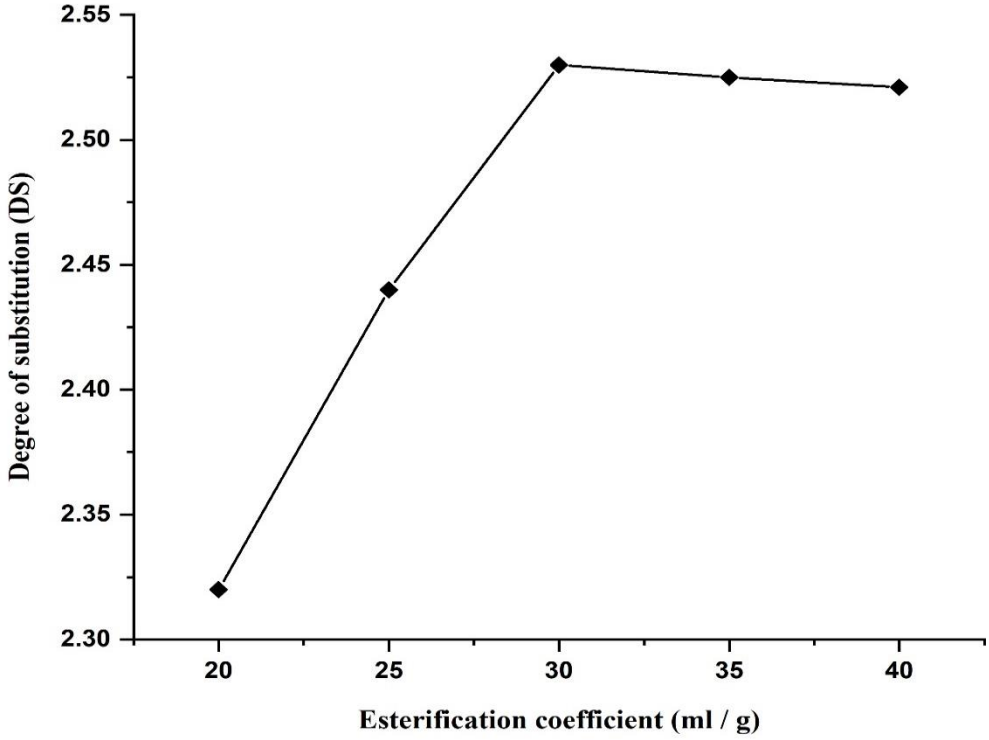


Figure 4.7: Effect of esterification coefficient on degree of substitution

Figure 4.7 shows the effect of the esterification coefficient on the degree of substitution at which its effect should be considered when the esterification coefficient is less than 30, especially for the synthesis of low degree of substitution values. But, as the esterification coefficient was increased beyond 30, the increase in the degree of substitution became insignificant and diminished; rather, it would affect the final cost of production.

4.6.6.2. Effect of sulfuric acid to nitric acid ratio on DS of nanonitrocellulose

The effect of sulfuric acid to nitric acid ratio on the degree of substitution (DS) was investigated to determine the best combination of the acids required for nitration of nanocellulose for obtaining the desired nitrogen content of the synthesized nanonitrocellulose. The samples of nanocellulose were nitrated by using a 30 ml/g esterification coefficient, a 40 min nitration time, and a 30 ℃ nitration temperature, and the ratio of sulfuric acid to nitric acid was varied from 2.4 to 3.6 with 0.2 increments.

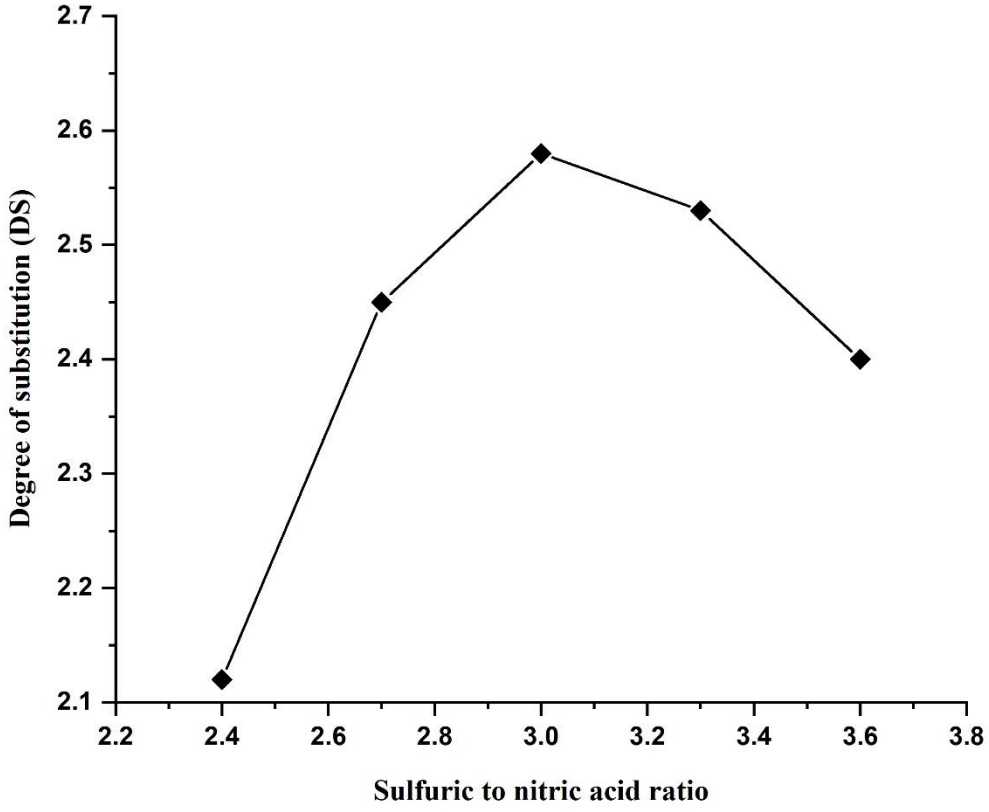
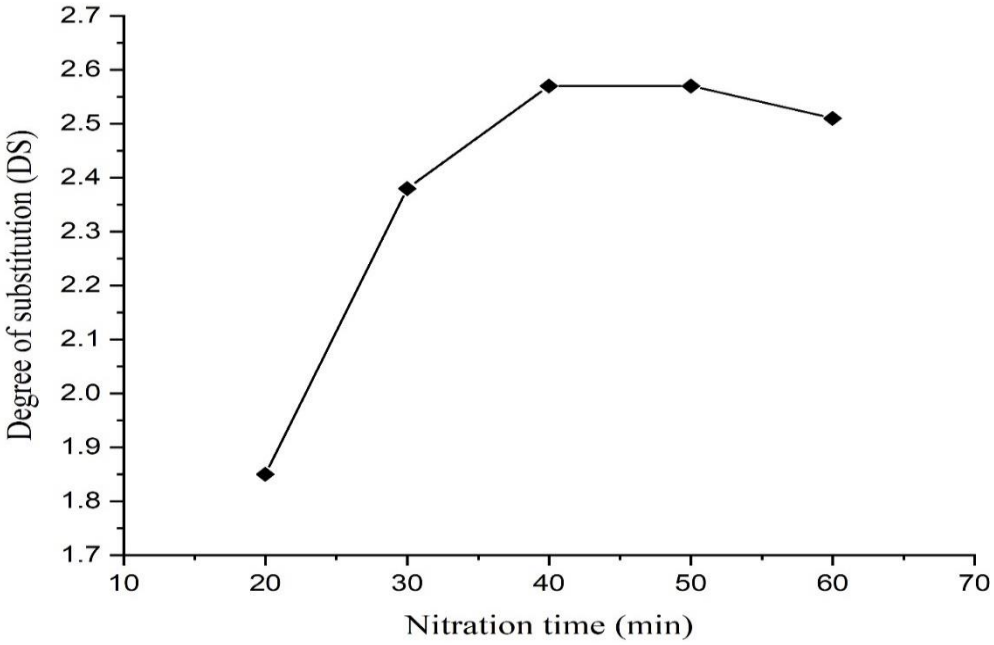


Figure 4.8: Effect of sulfuric to nitric acid ratio on degree of substitution

Figure 4.8 shows that when the sulfuric acid to nitric acid ratio is in the range of 2.4–3.0, the degree of substitution (DS) is increasing to its maximum. When the ratio of sulfuric acid to nitric acid is greater than 3.0, the degree of substitution (DS) decreases significantly, which is in agreement with the study reported by (Morris et al., 2023). Typically, having a higher content of sulfuric acid in the mixed acid results in the formation of more sulfate and severe nitration degradation. Early equilibrium experiments provide additional evidence that the proportions of these acids are crucial for the synthesis of nitrate esters (Housecroft, 2023). To minimize the consumption of nitrating acid and ensure the quality of the synthesized nanonitrocellulose, the ratio of sulfuric acid to nitric acid should be controlled in the range of 2.6–3.2.

4.6.6.3. Effect of nitration time on DS of nanonitrocellulose

The reaction time plays a crucial role in controlling the desired degree of substitution during nanonitrocellulose synthesis. The experiments on nanocellulose nitration with an increase in



nitration time from 20 to 60 min at an initial esterification coefficient of 30 ml/g and a 3.0 ratio of sulfuric acid to nitric acid at 30℃ were carried out as shown in Table 3.1**.**

Figure 4.9: Effect of nitration time on degree of substitution

According to the results presented in Figure 4.9, the nitration time has a certain effect on the degree of substitution (DS) of the synthesized nanonitrocellulose. The degree of substitution of the

synthesized nanonitrocellulose is almost linearly increased during the first 20-30 min of nitration and reaches a state of equilibrium, which aligned with the previous study (S. H. Jamal et al., 2019). When the nitration time proceeds from 40-50 minutes or beyond that, the effect on the degree of substitution (DS) is negligible since extended nitration time increases the likelihood of side reactions (Josmi John et al., 2024). Therefore, the effect of nitration time on the desired degree of substitution (DS) should be considered when the nitration time is between 40 and 50 minutes or less.

4.6.6.4. Effect of nitration temperature on DS of nanonitrocellulose

The temperature at which the nitration reaction was conducted has a crucial effect on the degree of substitution (DS) of the resulting nanonitrocellulose. The nitration of water hyacinth based nanocellulose experiments were conducted for 40 minutes at an esterification coefficient of 30 ml/g and sulfuric to nitric acid ratio of 3.0, with varied nitration temperature from 20 – 40℃ at specifically 20℃, 25℃, 30℃, 35℃, and 40℃ as shown in Table 3.1.

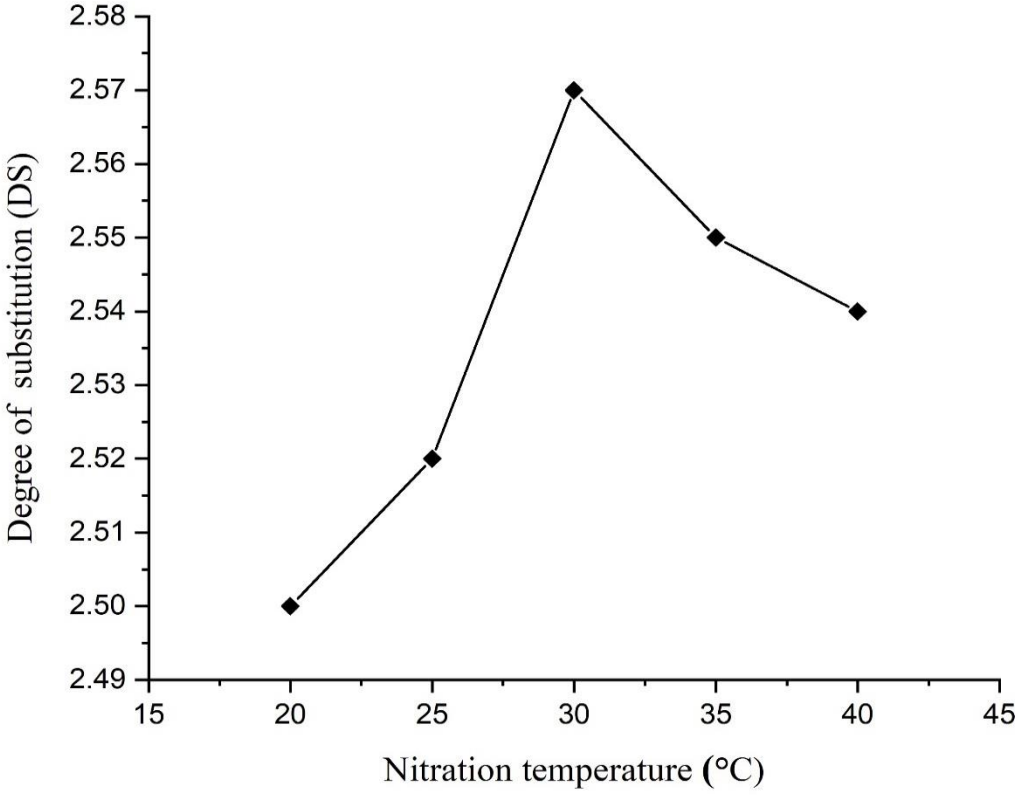


Figure 4.10: Effect of nitration temperature on degree of substitution

As shown in Figure 4.10, the degree of substitution (DS) increases when the nitration temperature of the nanocellulose is increased from 20 to 30. But as the reaction temperature increases beyond 30℃ the degree of substitution (DS) declines. This is due to the rise in temperature, which also results in the degradation of nanocellulose and side reactions such as hydrolysis and oxidation of the product, as described by (Josmi John et al., 2024).

4.6.7. Energetic performance evaluation for the synthesized nitrocellulose nanocrystal

The energetic performance of the synthesized nanocrystalline nitrocellulose was evaluated by using different parameters. One of the key parameters used in this study is determining its calorific value by using a bomb calorimeter and obtaining 10.04 KJ/g for a nitrated product with a degree of substitution (DS = 2.58), which is possible to use for propellant formulation. The differential scanning calorimetry (DSC) also showed high specific heats of decomposition (9.72 kJ/g) from the area of heat flow versus time data plot, which validated its calorific value (10.04 KJ/g) as determined by the bomb calorimeter and its energetic property. This energy value is sufficient beyond enough to produce pressure for propellant application, and this result is comparatively similar to other studies (Lemieux & Prud'Homme, 1985; Jessup & Prosen, 1950; J. Liu & Chen, 2018; Korchagina, et al., 2019) .

The obtained great density (1.842 g/cm^3) and elevated nitrogen content of 12.99% (DS = 2.58) is also another energetic evaluation parameter, according to described by (Moniruzzaman et al., 2011) at which nitrocellulose with nitrogen contents above 12.2% is used as an energetic ingredient in gun and rocket propellants.

5. CONCLUSSIONS AND RECOMMENDATIONS

5.1. Conclusions

To conclude, the synthesis of nanonitrocellulose from water hyacinth involves the extraction of nanocellulose present in the water hyacinth and introducing nitro groups through a nitration reaction. Nanocellulose of an appropriate quality for nitration was isolated from water hyacinth using Soxhlet extraction, alkaline treatment, bleaching, acid hydrolysis, and sonication steps to get a yield of 34.6% and an average diameter of 91.3 nm. It was found that high-quality nanonitrocellulose having 10.57–12.99% of the mass fraction of nitrogen with a respective calculated degree of substitution (DS) of 1.85–2.58 was produced by nitrating with a mixture of nitric and sulfuric acid from a lignocellulosic feedstock, water hyacinth. FTIR spectroscopy detected the basic functional groups of cellulose in the original raw water hyacinth, bleached cellulose, and nanocellulose samples, and the basic functional nitro groups in the synthesized NCNC. This result is in agreement with the XRD's result that the crystallinity index of raw fiber at the acid hydrolysis stage increased due to the removal of a non-cellulosic component. The crystallinity index of raw water hyacinth fiber, bleached cellulose, and acid hydrolyzed with ultrasonic homogenizing was 22%, 54%, and 76%, respectively. SEM microscopy showed that the chemical treatment affects the morphological structure of the fibers with respect to surface smoothness and size, and the resultant NCNC retained substantially the shape of the original nanocellulose with increased volume. TGA/DSC analyses also showed that the synthesized NCNC sample has a high purity and a high specific heat of decomposition of 9.72 kJ/g, which confirmed its energy capacity. In the case of nanonitrocellulose, elemental analysis and differential scanning calorimetry (DSC) provide important information about its energy content and potential application areas, including the development of propellants, explosives, and other energy-related materials. These findings suggest that water hyacinth-derived nanocrystalline cellulose nitrate, which has considerable potential for use in propellants, gas generators, and other industries, can be seen as a new, high-tech alternative to conventional cotton-based cellulose nitrate. In addition, water hyacinth is known for having a severe impact on both society and the environment. However, in this study, its potential as a feedstock for nanonitrocellulose synthesis has shown considerable value.

5.2. Recommendations

This study tried to deal with the synthesis and characterization of nano-energetic biopolymers from lignocellulosic feedstock (water hyacinth) through the extraction of nanocellulose and the respective nitration methods for the first time. If further research is going to be done in this area, the following points should be taken into consideration:

- In this work, nanocrystalline cellulose nitrate (NCNC) is synthesized by extracting nanocellulose (NC) from water hyacinth and nitration through a mixture of nitro-sulfuric acid, and the effects of sulfuric acid to nitric ratio, reaction temperature, and reaction time on the value of the DS of NCNC were discussed. The synthesized NCNC was well characterized by using SEM, FTIR, a nitrogen content analyzer, calorific value, and thermal analysis (TGA-DSC). However, it needs further characterization, such as burning rate and sensitivity test for further nano-energetic applications.
- The stability of the synthesized NCNC must be considered for long term storage. Therefore, it is recommended to perform by taking the samples having a certain period of storage lifetime.
- It is also recommended to perform an economic feasibility study and establish an economic scale for nanonitrocellulose production from water hyacinth.

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APPENDICES

Appendix A: DLS analysis of cellulose nanocrystal

Sample Details

Sample Name:	nanocellulose 1
SOP Name:	mansettings.nano
General Notes:	

File Name:	CNC.dts	**Dispersant Name:**	Water
Record Number:	9	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	Monday, Dec 4, 2023 5:...

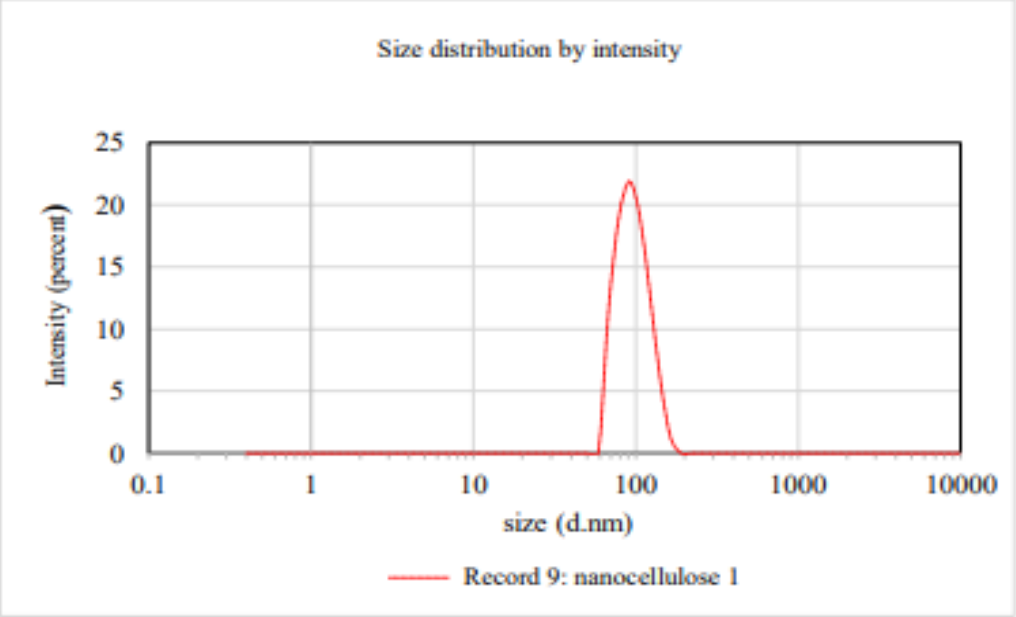
System

Temperature (°C):	25.0	**Duration Used (s):**	50
Count Rate (kcps):	49.0	**Measurement Position (mm):**	0.85
Cell Description:	Disposable sizing cuvette	**Attenuator:**	11

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d. nm):	85.72	**Peak 1:**	91.3	100.0	28.09
PdI:	0.327	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.891	**Peak 3:**	0.000	0.0	0.000

Result quality: good



Appendix B: Group Frequencies for Organic Functional Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left(\rangle C{=}C\langle^{H}\right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong