Journal of Advanced Engineering Trends
ISSN : 2682 - 2091

Vol.43, No.2. July 2024

http://jaet.journals.ekb.eg

Nanocellulose preparation, production modeling and characterization

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ARTICLE INFO

Article history:
Received:
Accepted:
Online:

Keywords:
Analysis
Biomass
Nanocellulose
Scale-up
Visual Basic.NET

ABSTRACT

Biomass is any organic material derived from plants or animals on our planet. Nanocellulose is cellulose provided in nano-sized particles from biomass (NC). It is a promising potential biomaterial with considerable applications in the pharmaceutical and biological industries. The experimental setup procedures and equipment for generating NC on a lab scale were carried out. The obtained NC was analyzed using characterization techniques. NC was assessed using a scanning electron microscope, Fourier-transform infrared spectroscopy, and a particle size analyzer. Developers can use programming tools to create, write, test, and debug other software applications. This study presents software for NC production design. The software was designed to scale up production on a pilot scale and determine reactant quantities based on an NC production rate. Before expanding our use of these materials, we evaluated the materials and techniques utilized in NC manufacture on a lab scale. It is necessary to enter the production rate as well as the experimental parameters, which are acid concentration and reaction temperature in hydrolysis.

1. Introduction

Biomass refers to any organic material derived from plants or animals that were living in the past. [1] Solid biomass is not the only type of biomass that can be found. Examples of biomass include fats, grease oils, etc. lignocellulose is a significant component of biomass.[2] There are more details about this type now. The non-starch, fibrous part of the plant is lignocellulosic material.[3 , 4]

Even though the polymeric composition of a biomass's cell walls and other constituents can vary widely, the three significant polymers that make up biomass are generally thought to be cellulose, hemicellulose, and lignin.[5 – 7]

As the most abundant organic compound on the planet, cellulose serves as a primary structural component of plant cell walls in biomass. It has a bioproduction estimated to be over $7.5*10^5$ metric tons annually[8 – 10].

Revised:25 August , 2022, Accepted:16 October , 2022

It is widely distributed over a variety of sources, including marine animals (e.g., tunicates), plants (e.g., wood, cotton, or wheat straw), and bacterial sources, such as algae (e.g., Valonia), fungi, and even amoeba (protozoa)[11 – 13]. Various methods can be used to obtain Nanocellulose (NC), such as acid hydrolysis, ultrasonic technique, and enzymatic hydrolysis.[14 , 15] The method that most widely used is acid hydrolysis [16 – 18]. In addition to being biodegradable, NC has a low density and good mechanical properties.[10]

According to several studies, the crystallinity index of acid hydrolyzed NC was discovered to be significantly higher than that of various other methods. NC with a smaller diameter is produced due to the acid hydrolysis.

The acid hydrolysis method was selected to be used in the production of NC. [19 – 21]

Glycoside bonds in cellulose are commonly broken using strong acids like H_2SO_4 and HCl. Acid hydrolysis involves several steps: (1) strong acid hydrolysis of cellulose under controlled conditions, such as acid concentration, time, temperature, and acid-to-cellulose ratio; (2) dilution with some water to stop the hydrolysis process and repeated washing with successive centrifugation; (3) dialysis to remove all free acid molecules; (4) sonication to form a stable NC suspension; (5) drying of the suspension to yield solid NC.

A developed tool was named efficient production technologies (EffTech) research program in Forestcluster Ltd.

They describe structural, mechanical and optical properties of paper-like structures based on particle-level models, which cover materials and structures from nano to macro scale, i.e., from atomistic simulations to macroscopic product properties.[22]

This will cause a big challenge for the traditional way of development work, which is based almost solely on laboratory experiments, pilot and full-scale testing. Virtual product modeling offers a way to significantly speed up product development. Understanding the effect of NC and associated processes on final product properties requires multi-scale analysis. [22]

In this work, we produced the NC by acid hydrolysis using sulfuric acid H_2SO_4. In addition, we performed characterization for the product by Scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and Particle sizer analyzer (PSA).

Furthermore, we created a computer-aided program to calculate scale-up production and reactor design dimensions. The software was developed by the Visual basic.NET platform with a free license for programming desktop software.

2. Materials and Methods

2.1. Materials

Pulp was kindly supplied from Pulp and Paper Masr Company, Edfou, Aswan, Egypt. (the analysis of raw material is presented in Table 1)

Sulfuric acid H_2SO_4 was purchased from El-Gomhouria Pharmaceuticals and Chemicals Company, Cairo, Egypt and used for the hydrolysis processes.

Table 1:: Characterization for Semi-Kraft Pulp manufactured by Masr Edfou, Egypt

Properties	Values
Cellulose %	97-98%
Ash, Lignin and Chemical Residual	2-3%
Degree of Polymerization (DP)	810
Bulk Density	1.4 g/Cc

2.2. Methods

2.2.1 Preparation of Nanocellulose crystals (NCC)

An aqueous suspension of NC was prepared by hydrolysis process as shown in Figure 1. Free cellulose obtained in Pulp was acid hydrolyzed by refluxing with 60% (w/w) sulfuric acid (Pulp to liquor ratio of 1:20) for 120 min at 50 ◦C under strong agitation. The hydrolysis was quenched by adding (100 ml) distilled water to the reaction mixture. The resulting mixture was cooled to room temperature and centrifuged. The fractions were continuously washed by the addition of distilled water and centrifuged.[23 – 25]

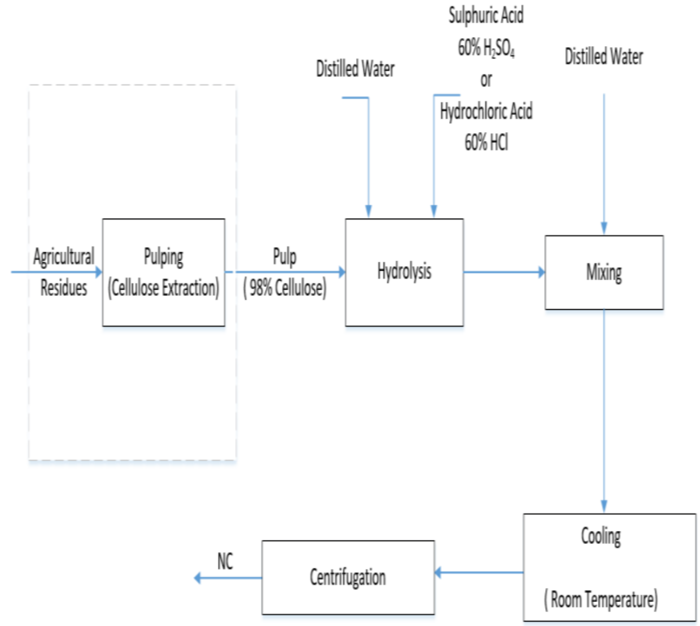

Figure 1: NC manufacturing block flow diagram from pulp

2.2.2. Production modeling of NC

A computer aided software was coded for determining quantities of reactants concerning the production rate of NC. The user interface's inputs in production software represent the Pulp mass, acid concentration, initial temperature of reaction, and the type of acid. For this reason, the mathematical model is a multi-equation system.

In Figure 2, Users are required to enter the production rate and the experimental conditions, which are acid concentration, acid type, and temperature of reaction applied in hydrolysis.

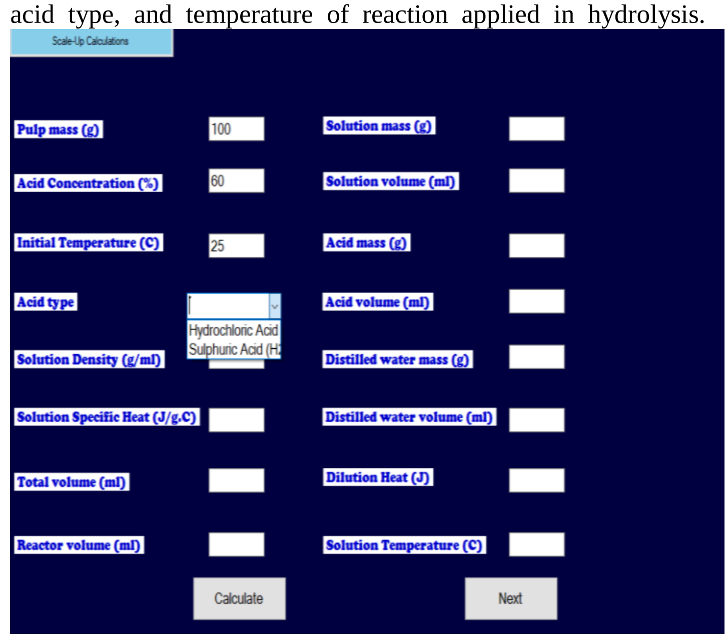

Figure 2: User input interface for reactants in pilot plant production of NC

The amounts for each reactant are calculated in pilot-scale volume, ranging from 1 to 100 L. These amounts are defined with respect of Pulp mass entered in the following equations (1-5).

$$Solution\ mass = \frac{Pulp\ mass}{Pulp\ to\ liquor\ ratio} \quad (1)$$

$$Acid\ mass = Solution\ mass * \frac{\text{Acid Concentration (\%)}}{100} \quad (2)$$

$$Acid\ volume = Acid\ mass * \rho_{Acid} \quad (3)$$

$$Distilled\ water\ mass = Solution\ mass * \frac{(100 - \text{Acid Concentration (\%)})}{100} \quad (4)$$

$$Distilled\ water\ volume = Distilled\ water\ mass * \rho_{Distilled\ water} \quad (5)$$

The scale-up production procedures involve determining the vessel's internal geometry. These dimensions are shown in Figure 3 based on the volume of reactants with usable volume of 80%, which are calculated with the standard recommendations.

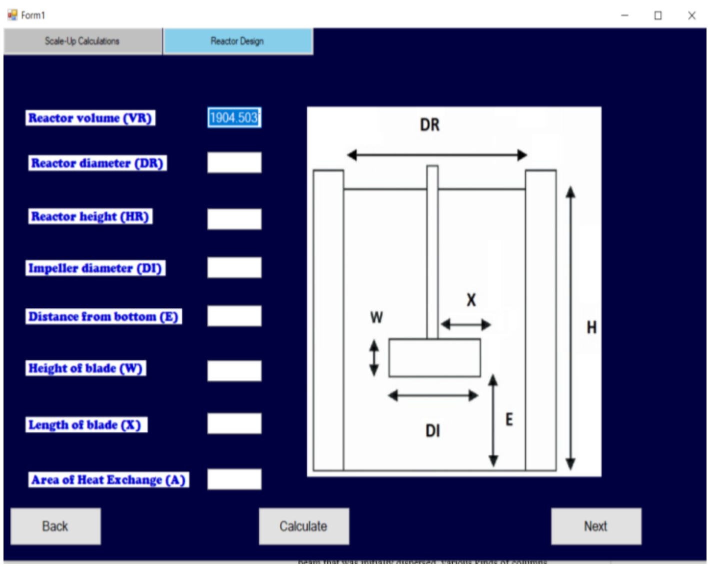

Figure 3: Reactor design specifications for production of NC

Vessel specifications

This procedure involves the determination of the vessel's internal geometry, which will be calculated from the standards recommended by Rushton et al.[26]

- Volume of Tank (V) is defined within the equation (6).

$$V = \frac{\pi}{4} * D_t^2 * H \quad (6)$$

$$\because D_t = H$$

$$\therefore V = \frac{\pi}{4} * D_t^3$$

By applying the geometrical relationship [$D_t = H$] in equation (1), we obtain the following equation (7).

$$\therefore D_t = \sqrt[3]{\frac{4 * V}{\pi}} \quad (7)$$

Impeller's specifications

- Type: axial impeller and four blades inclined by 45°.
- Diameter of impeller (D_a) can be calculated by following equation (8).

$$D_a = \frac{1}{3}(D_t) \quad (8)$$

- Distance of impeller from bottom (E) is obtained by following equation (9).

$$E = D_a \quad (9)$$

- Height of blade impeller (W) is calculated within following equation (10).

$$W = \frac{1}{5}(D_a) \quad (10)$$

- Length of blade impeller (X) can be achieved by the following equation (11).

$$X = \frac{W}{0.707} \quad (11)$$

2.2.4. Characterization Techniques

SEM ,FTIR, and PSA were used to examine the material's internal and external structure and surface properties. In order to identify the adsorbent's composition, we used SEM JSM 6510 LA (JEOL), FTIR Prestise-21 (Shimadzu) to identify functional groups, and PSA (Nano-ZS, Malvern Instruments Ltd., UK) to calculate the average diameter, the size distribution, and zeta potential of samples were measured by using a particle size analyzer.

Fourier transform infrared spectroscopy

The technique known as Fourier transform infrared spectroscopy, or FTIR for short, is a method that can be used to obtain an infrared spectrum of the absorption, emission, and photoconductivity of a solid, liquid, or gas sample. It is utilized in the process of determining the various functional groups present in NC. Recording of the FTIR spectrum takes place between 4000 and 400 cm^{-1}.

Scanning electron microscope

The technique involves moving an electron beam across a sample in a series of lines that are parallel to one another in order to obtain an image at the desired level of magnification. The electron beam is created in a column of high vacuum, and the electrons themselves are produced by the heating of a filament made of tungsten, lanthanum hexafluoride, or some other material.

Particle size analyzer

Particle size analysis was carried out using Malvern Master Sizer 2000. This analysis is performed only for samples of domestic wastewater influent and effluent.

Each sample has been diluted with ethanol. Particle size distributions in the sample are recorded as volume percent in size ranges between 0.01 to 2000 µm.

3. Results and Discussion

3.1. Preparation of Nanocellulose (NC)

Figure 1 depicts the experimental setup procedures that must be followed in order to produce NC on a lab scale. These producers are converted into units to be used in the NC production which take place in the pilot plant. Every unit is taken account for the rest of the calculations in the software code. The essential parts of the manufacturing of NC are presented in Table 2.

Table 2: Basic units for NC pilot plant production

Unit	Material of Construction
Reactor	Stainless Steel (St.St.)
Mixer	St.St.
Cooler	St.St.
Centrifugation unit	St.St.
Dryer	St.St.
2 Storage Tanks	St.St.
Regenerator	St.St.

The usage of acids in the production of NC was researched in relation to the material of construction that was being looked into. This is because the acids that are employed in the procedure have characteristics that make them corrosive. In addition, the usage of the heat generated during acid diluting is considered in the pilot scale.

3.2. Production modeling of NC

The mass of pulp, the acid concentration, the initial temperature of the reaction, and the type of acid are all represented as inputs in the production software. The software was coded for determining quantities of reactants with regard to production rate of NC. Figure (4) demonstrates the programming code concerning the percentage for each material. In fact, users are required to enter the production rate and the condition experimental conditions which are acid concentration and temperature of reaction applied in hydrolysis.

Figure 4: Software calculation for reactants in pilot plant production of NC

The reactor specifications are shown in Figure 5 was developed with the proper dimensions in accordance with the guidelines. This allowed the equations to be applied to the design process, which took into account the volume of materials that were engaged in the reaction. Table 2 displays the rounded versions of the findings returned from running the software, which were done thus to make the result more acceptable.

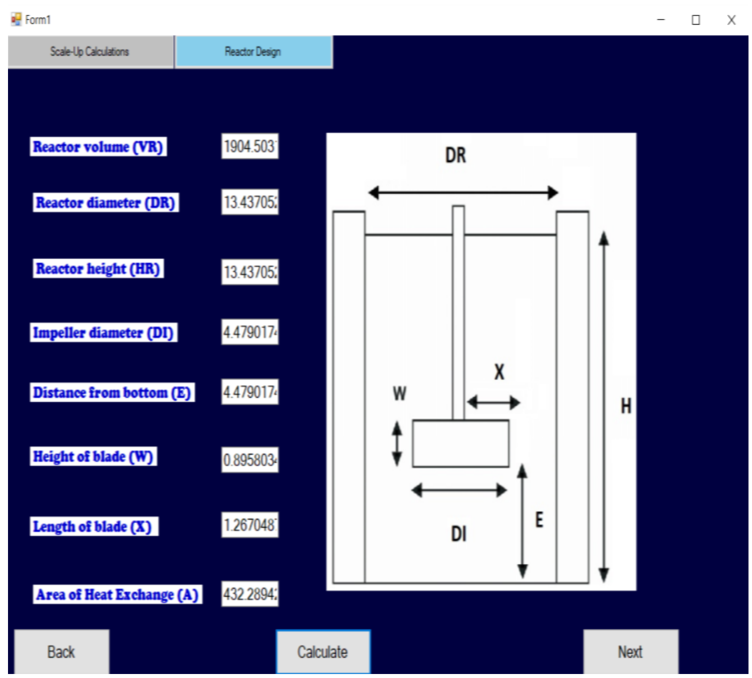

Figure 5: Reactor specifications for NC production

Table 3: Reactor specifications for NC production

Specification	Approximated values
Reactor Volume (VR)	2000 (cm^3)
Reactor Diameter (DR)	13.5 (cm)
Reactor Height (HR)	13.5 (cm)
Impeller Diameter (DI)	4.5 (cm)
Distance from bottom (E)	4.5 (cm)
Height of blade (W)	1 (cm)
Length of blade (X)	1.5 (cm)
Area of Regenerator (A)	433 (cm^2)

3.3. Characterization Techniques

FTIR analysis has done to indicate the functional groups of NC produced. In Figure 6, the adsorption peak around 3434.67 cm^{-1} indicates the existence of free hydroxyl groups. The C-H stretching vibration around 2925.66 cm^{-1} indicates the presence of alkane functional group. The C-O bond is referred by the peak of 2372.42 cm-1. The peaks around 1628.72 cm^{-1} correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups. The peaks around 1168.61-1036.55 and 881.16-582.96 cm^{-1}, corresponds to CH-OH stretching, Si-O-Si stretching and Si-H groups, respectively.[23]

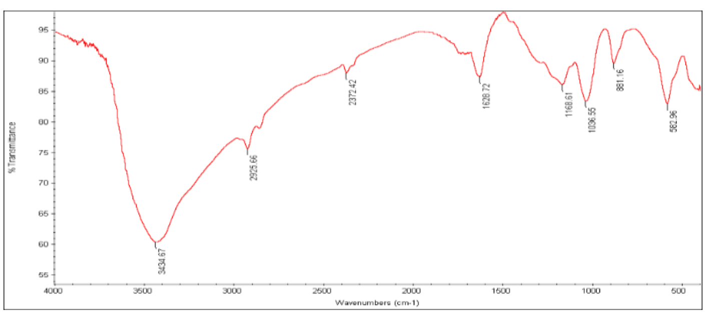

Figure 6: FTIR analysis for NC

The morphology measurements of the NC were carried out on a SEM which is shown in Figure 7. a. Dimensions of extracted NC was obtained by SEM image analysis. It ranges between 79-529 nm. Particle size distribution of NC produced from semi-kraft pulp is presented in Figure. b. [23]

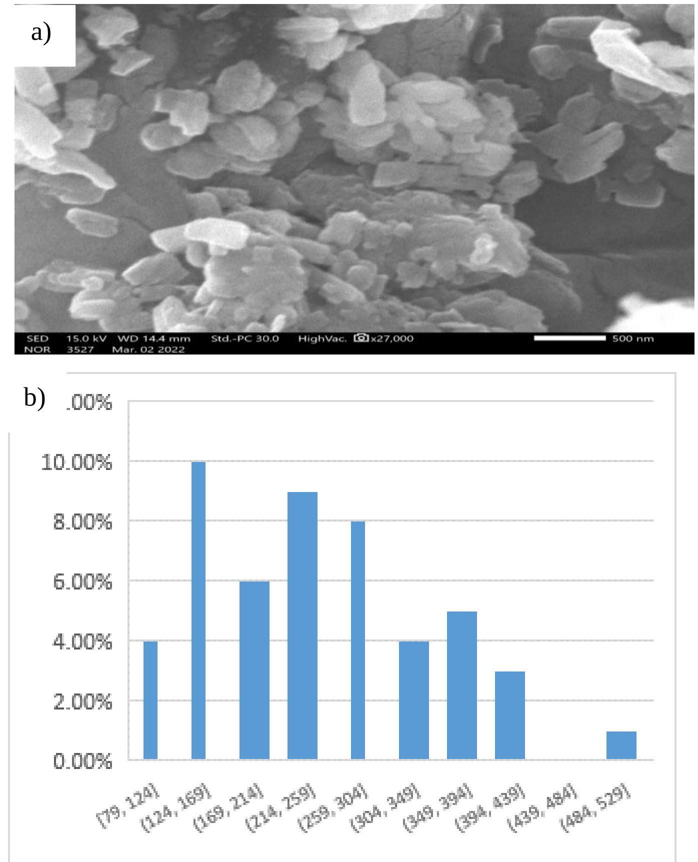

Figure 7: a) SEM analysis for NC, b) Particle size distributions (PSD)

By performing an analysis on the sample, the particle size was obtained for the sample as well as its distribution. This was similar to the SEM image. since we were able to determine how the sample was distributed. The range of the particles size varies from 100 nm to 280 nm.

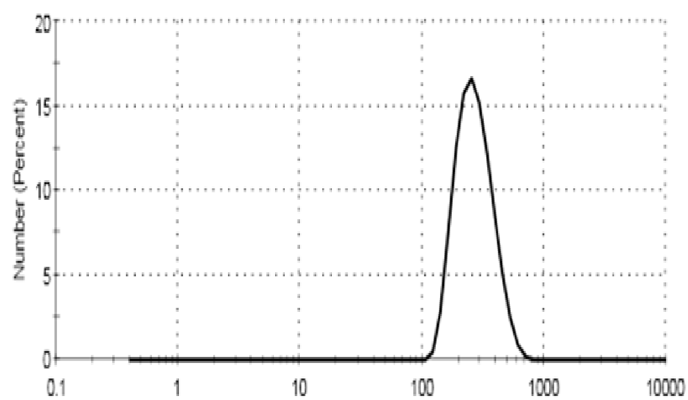

Figure 8: PSD for NC by particle size analyzer

4. Conclusions

NC successfully synthesized from locally pulp manufactured from sugarcane residues. In addition, the experimental setup procedures and assembled the necessary equipment to produce NC on a lab scale were carried successfully.

Characterization techniques were used to determine the characteristics of the NC that was obtained. For the purpose of evaluating NC, SEM, FTIR and PSD. The SEM image of prepared NC showed the range of particle size. This range indicates the Nano-scale of Cellulose that has located in the range from 57 to 1100 nm in length and 0.1 to 145nm in diameter[27] . The range of the particles size was verified by PSD analysis. The particles vary from 100 nm to 280 nm.

This research presents a software that can be used for designing the production of NC. The software was correctly programmed to allow for scaling up production for pilot-scale production as well as determining the quantities of reactants necessary in relation to the rate of production of NC. Before increasing the quantity of these materials, we conducted an investigation on a smaller scale into the processes and components that are utilized during the production of NC. It is necessary to enter both the production rate and the experimental conditions, which include the concentration of acid and the temperature of the reaction when hydrolysis is being carried out.

The specifications of the reactor are depicted in the research. These specifications were produced with the appropriate dimensions in compliance with the standards. This made it possible to apply the equations to the design process regarding to the quantity of materials that were involved in the reaction. The results that were produced by the software after it was run, along with rounded versions of those findings.

Using the acid hydrolysis method and sulfuric acid H_2SO_4, NC was synthesized in this study. A study conducted in the manufacturing of NC regard to the construction material. Using acids with corrosive property must be taken into consideration for pilot plant construction. In addition, the pilot scale takes into account the use of heat created during acid diluting.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

There is no fund has been received for conducting the research.

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Abbreviation and symbols

NC	**Nanocellulose**
EffTech	**Efficient production technologies**
FTIR	**Fourier transform infrared spectroscopy**
SEM	**Sransmission Electron Micrograph**
PSA	**Particle Sizer Analyzer**
St.St.	**Stainless Steel**
PSD	**Particle size distributions**