Chemical and Biological Pretreatment Process of Energy Efficient Manufacturing of Nanocellulose

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Abstract

Nanocellulose is a new-age substance derived from cellulosic biomass and has huge exact surface area, high modulus and extremely hydrophilic in nature. It comprises of two structural forms viz., nano fibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). This paper provides an important summary of the recent methods of bio- and chemo-mechanical processes for construction of nanocellulose, their energy requirements and their functional properties. More than a dozen of pilot plants/commercial plants are under operation mostly in the urbanized countries, trying to develop the probable of nanocellulose as reinforcing agent in paper, films, concrete, rubber, polymer films and so on. The exploitation of nanocellulose is classified mainly due to preliminary asset involved, high manufacture cost and require of toxicological information. This paper focus the present development and exploration of power proficient and environment using pretreatment their possibility in scaling up and the potential range for growth of nanocellulose application in various fields without impacting the atmosphere. In accumulation, a nanocellulose quality index is derived to act as a guide for appliance based screening of nanocellulose creation protocols.

Keywords: *Biodegradable, Energy Conservation, Mechanical Process, Nanocellulose, Pretreatment.*

I. INTRODUCTION

Nanocellulose is a word referring to nano-structured cellulose. This may be moreover cellulose nanofibers (CNF), nanocrystalline cellulose (NCC or CNC), which refers to nano-structured cellulose produced by bacteria. CNF is a substance collected of nanosized cellulose fibrils with a high aspect ratio. Characteristic fibril widths are 5–20 nanometers with a large array of lengths, naturally several micrometers. It is pseudo-plastic and exhibits thixotropy, the property of firm gels or fluids that are thick under normal conditions, but become less glutinous when surprised or anxious. When the shearing forces are removed the gel regains much of its original state. The fibrils are unreachable from any cellulose containing source including wood-based fibers through persuasive, high warmth and high speed impact homogenization, grinding or micro fluidization.

Nanocellulose can also be obtained from native fiber by an acid hydrolysis, giving rise to highly crystalline and rigid nanoparticles which are shorter than the nanofibrils obtained during homogenization, micro fluidization or grinding routes. The ensuing material is known as nanocrystalline cellulose (NCC or CNC).

II. CELLULOSE

Cellulose is a usual biopolymer prepared up of linear chain of several hundred to over ten thousand ß linked D-glucose, having the formula $(C_6H_{10}O_5)n$ and stabilized by intermolecular hydrogen bonds. It is a crystalline structural polysaccharide and the most plentiful form of living earthly biomass available on Earth. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff-chain homopolymer is characterized by its hydrophilicity, chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semi crystalline fiber morphologies.

This paper focused on new frontiers, including environmentally friendly cellulose fiber technologies, bacterial cellulose biomaterials, and in vitro syntheses of cellulose together with future aims, strategies, and perspectives of cellulose research and its applications. The current three kind of hydroxyl groups within an anhydroglucose unit in a cellulose molecule display dissimilar polarities, which donate to formation of various kinds of inter- and intra-molecular hydrogen bonds among secondary "-OH" at the C-2, secondary "-OH" at the C-3 and primary "-OH" at the C-6 position. In addition, all the hydroxyl groups are bonded to a glucopyranose ring equatorially. This causes manifestation of hydrophilic site parallel to the ring plane. On the contrary, the "CH" groups are bonded to a glucopyranose ring axially, causing hydrophobic site perpendicular to the ring. These effects lead to formation of hydrogen bonds in parallel direction to a glucopyranose ring, and to van der Waals interaction perpendicular to the ring.

Cellulose occurs in nearly the purest form in cotton fibers, while in wood and various parts of plants, it is found in mixture with other materials, mostly lignin and hemicelluloses. Cotton fibers are of great interest as they lack lignin, which minimizes number of processes during manufacturing of nanocellulose. Cellulose is also produced by bacteria, algae, fungi and tunicates. Figure 1 shows the schematic representation of structural arrangement of cellulose microfibrils in cottonfibers.

III. NANOCELLULOSE

Nanocellulose represents a new family of nanomaterials that emerge to have very broad applications in a variety of materials related domains where physical characteristics such as strength, weight, rheology, optical properties and the like can be affected in a very positive manner. Acronyms commonly used to denote nanocellulose include cellulose nanocrystals (CNC), nanocrystalline cellulose (NCC), cellulose nanoparticles (CNP), microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC). A recommendation on the preliminary terminology framework for nanocellulose was presented at an initial TAPPI's workshop held in Arlington on 9th June 2011 as given in Figure 2. In this categorization, cellulose nanofibrils and cellulose microfibril are classify individually that we feel is puzzling since it is very much difficult to discriminate these two materials by asset of their overlapping in properties. While few researchers categorize bacterial cellulose as a type of nanocellulose, it is beyond the scope of this paper and hence, not included here. Hence, in this paper, nanocellulose is classified only as two groups viz., Nanocrystalline cellulose (NCC) having low aspect ratio (<100) and Nanofibrillated cellulose (NFC) having high aspect ratio (>100).

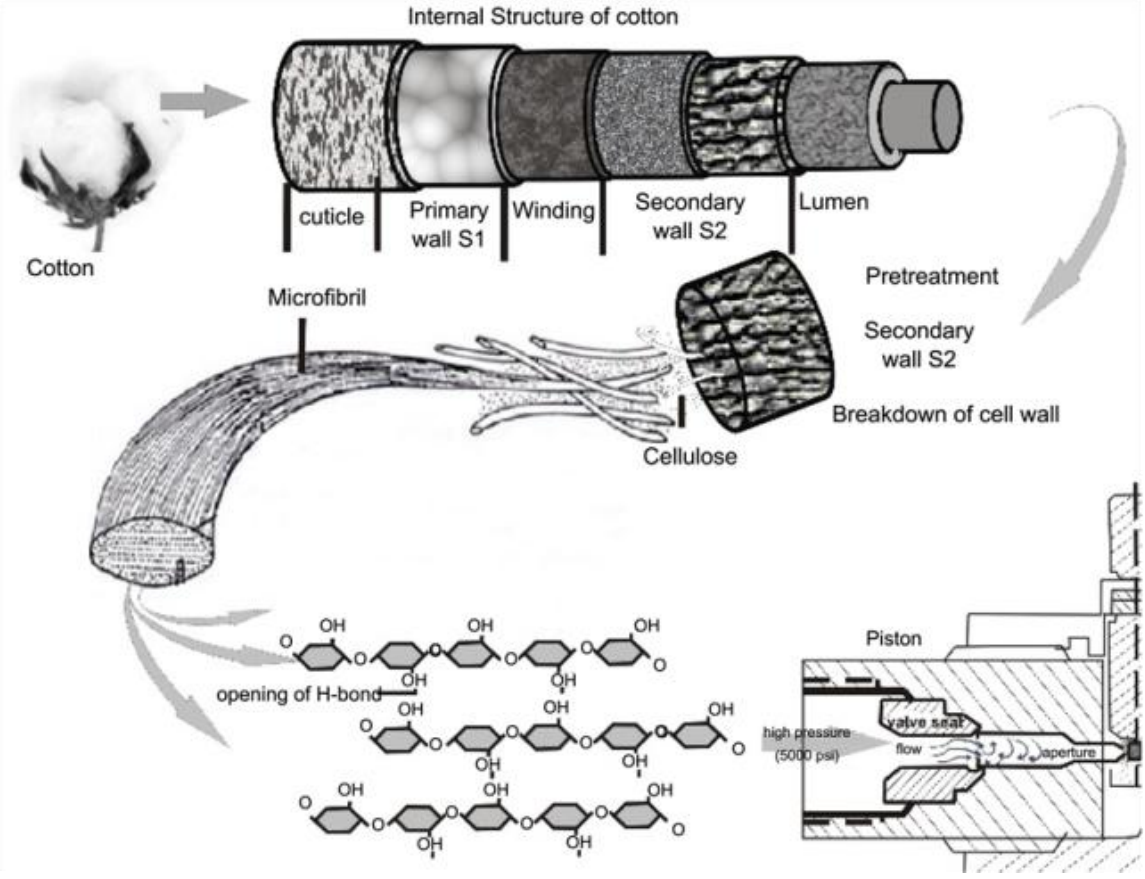

Figure 1. Schematic Representation of Structural Arrangement of Cellulose Microfibrils in Cottonfibers.

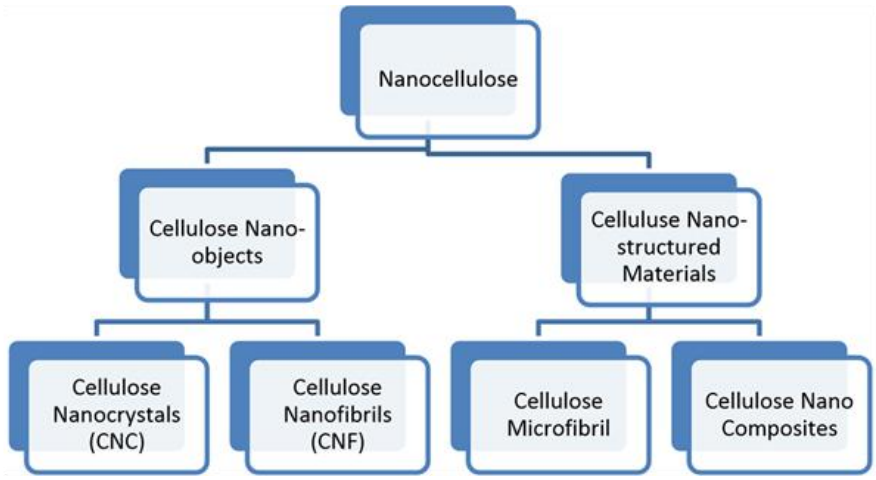

Figure 2. Naming Hierarchy of Nanocellulose as Per the TAPPI's Workshop Held in Arlington On 9th June 2011.

A. Structural Properties of Nanocellulose

The nanocellulose is the minimum structural part of the cellulosic biomass of a variety of organisms. While NFC is normally shaped by automatic process, NCC is by concerted acid hydrolysis. Hence, the NFC is extra in amorphous nature when compared to NCC. These basic structural differences lead to dissimilar types of application for NFC and NCC.

The determination of stiffness by theoretical and experimental means has shown that native cellulose has a Young's modulus of 167.5 GPA and that of regenerated cellulose is 162.1 GPA. Using atomic force microscopy (AFM), various researchers evaluated the elastic modulus of both NCC and NFC. Self-standing TEMPO oxidized cellulose nanofibres are transparent and flexible, with high tensile strengths of 200 - 300 MPa and elastic moduli of 6 - 7 GPA. The high strength of nanofibrillar cellulose combined with its potential economic advantages offers the opportunity to make lighter and strong materials with greater durability. Indeed, because of these properties a nanofibre have attracted a lot of research effort in different disciplines and continues to be a subject of its utility in everyday materials such as paints, packaging, cosmetic bases, pigments, food modifiers, sensor applications, biomedical sciences and composites.

B. Reduction In Energy Consumption By Chemical Pretreatment

The result of a variety of substance pretreatments on power protection or condition for nanocellulose production is listed in the Table 1. Depending on the process and their analyses, the energy conservation/ requirement are listed in the references. The energy considered listening carefully only on the actual energy required for mechanical comminution process without including the energy required during chemical pretreatments. Hence, a fair comparison of energy conservation is not possible. Within the framework of EU-FP7 INNOBITE project, the Spanish applied research institute Tecnalia Research & Innovation and Ecopulp Finland Oy, a SME devoted to the production of shape moulded pulps out of waste paper, are developing a new method for converting waste paper into a new value-added material: newspaper- based nanocellulose. The aim is plummeting the energy needed for the paper fibrillation process, for which a specialty pulp is generated via oxidation reactions. This chemical treatment converts the hydroxyl groups at the native cellulose fibers into carboxylate groups, thus creating anionic charges that will subsequently turn into repulsion forces within the internal structure of the fibers. Combining Ecopulp's industrial facilities and Tecnalia's know-how, such a specialty cellulose pulp has already been produced in mid-scale. So far, the energy requirement for complete paper fibrillation has been decreased to values of 2.1 kWh per kilo of dry matter that equals the range of other extensively applied industrial treatments such as pulp refining.

C. *Reduction in Energy Consumption By Biological Pretreatment*

While chemical pretreatment results in substantial reduce of energy consumption, there explode the difficulty of waste removal and release of substance pollutants into the surroundings. Also, depending on the nature of the chemical treatment, the surface chemistry of fiber gets customized. To circumvent these problems, biological pretreatment shall be an ideal means of reducing power utilization without creating chemical effluents.

The high hemicellulose content of the pulp decreases the cell wall cohesion of the fibers, making cell wall delamination easier. But, this unaided was not sufficient to evade blocking of the orifice in the homogenizer and to reduce energy consumption. Hence, small additions of the mono-component endoglucanases enzyme promoted cell wall delamination and prohibited the blocking of homogenizer.

Table 1. Effect of Chemical Pretreatments on Energy Conservation/Requirement During Nanocellulose Production.

No	Pretreatments	Effect of pretreatments	Energy conservation Requirement	Process & remarks
1	(a) Ozone at a charge level of at least about 0.1 wt/wt%, based on the dry weight of the cellulosic material for generating free radicals in the slurry			
2	(b) Cellulose enzyme at a concentration from about 0.1 to about 10 lbs/ton based on the dry weight of the cellulosic material A combination of both (a) and (b) mentioned above	Partial depolymerization of cellulose	>2% energy conserved	Comminution processing
3	Organic (morpholine, piperidine or mixtures) or inorganic (inorganic halide, an inorganic hydroxide, or mixtures thereof) swelling agent or a mixture thereof	Swelling of cellulose	1400 kWh/t energy required 500 kWh/t energy required	Comminution processing 80% nanocellulose (defined as having an average diameter of less than 30 nm) 45% of the material having average diameters less than 30 nm
4	Carboxymethylation	Increases the anionic charges due to the formation of carboxyl groups in the surface	5500 kWh/t without pretreatment (per pass through)-Minimum of 4 passes 2200 kWh/t with pretreatment (per pass through)-4 passes 30000 kW/t (total) without pretreatment	Micro fluidization process Ultra-fine friction grinding

5	Carboxymethylation OR by irreversibly attaching CMC onto cellulose fibers	Increases the anionic charges due to the formation of carboxyl groups in the surface	500 - 2300 kWh/t	Micro fluidization process
6	Acid like sulfur dioxide, sulfurous acid, sulfur trioxide, sulfuric acid, lignosulfonic acid & their combinations or enzyme	Hydrolysis	<1000 kWh/t	Mechanical treatment

The bio-mechanical process overcomes the high energy obligation to a sure extent; however, the use of cellulose hydrolyzing enzymes also has a negative impact on the molecular weight and the chain length of the isolated nanocellulose. Hence, pretreatment with the expand secreting hydrogen bond-specific enzymes was tested to produce nanocellulose with mechanical strength marginally higher to that of those isolated via a conventional mechanical process since the bio-pretreatment produced nanocellulose had higher aspect ratio.

IV. CONCLUSION

In spite of various reports claiming reduction in energy consumption in nanocellulose manufacturing due to pretreatments, a holistic approach is required to include the energy equivalents of a variety of axillaries and other processes involved during such pretreatments. Energy utilization in terms of chemicals/enzyme equivalence, time required for pretreatments, quality of output subjected to pretreatments needs to be evaluated and used for contrast. Such a measure is possible in pilot plants/commercial plants of nanocellulose production. The optional nanocellulose excellence index will act as a guide for submission based transmission of nanocellulose construction protocols.

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