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Comprehensive Study of Nano Cellulose Lignocellulosic Bionano Material

Dr. Udai Pratap Singh
Assistant Professor,
Deptt. of Chemistry,
D. A-V. College, Kanpur

Abstract
There has been an explosion of interest in the use of biomass as a source of renewable energy and material. Nano technology has been advancing rapidly in recent yearsby attaining prominence as nano- structured material, in the form nanocellulose material.
The nanostructure of cellulose can play a significant part in pa- per making and high quality nano composites. It mainly consists of chemically cellulose nano crystals or mechanically extracted nanoparticles (micro fibrillated cellulose).
Nanocellulose based materials are neutral, sustainable, recyclable and non-toxic. They have the potential to be truly green nano materials with many useful and unexpected properties.
Nanotechnology based developements can provide incremental and evolutionary changes.A greater understanding of implications of using nanotechnology will ensure that nanotechnolgy is a valuable tool for our future.
Keywords: *Nanocellulose, lignocellulosic biomass, cellulose, hemi- cellulose, lignin*

I. INTRODUCTION

Too small to see but too big to ignore, nanotechnology is a new tool added in the recent years in a wide range of applications; pulp and paper is one of them. In recent years many research works have been carried out by researchers worldwide on the use of nanotechnology in many areas of technology. Nanotechnolgy is expected to be a critical driver of global economic growth and development in the near future. Already this extensive multidisciplinary field is pro- vided that glimpses of exhilarating new capabilities, empowering materials, devices and coordination that can be examined, engineered and fabricated at the nanoscale. Using nanotechnology to controlabally produce nanomaterials with exceptional properties is expect- ed to transfigure technology and industry. The aim of this paper is to show the developments in the field of pulp and paper industry, the potential of lignocellulosic material and nano cellulose synthesis.In this industry various developments in the field of nano cellulose has taken place. Thereis a motivating research workin the field of nano- cellulose. Nanocellulose, a wonderful material is synthesized from wood. Nanocellulose is made up of nanofibril. It has width less than 20 nm and has good strength.

A cellulose fiber is the material used for making paper.Other sources by which paper can be made are wood ragscellular hierarchicalbio- composites produced by nature, and they are essentially semi crystalline cellulose microfibrile reinforced amorphous matrices made of hemicellulose, lignin, waxes, extractives and trace elements. The pulp and paper industries aim to better utilize all components that are available in wood and wood based materials [1–6].

LIGNOCELLULSIC BIOMASS AND NANOCELLULOSE

Nanocellulose, which is obtained from cellulose is creating a revolution is biobased materials for diverse applications. Nanocellulose is having various characteristics which are nano scale dimension, high surface area, unique optical properties, highly crystalline, stiffness, biodegradability and renewability of nano cellulose. Due to its prop- erties this precious green alternative finds various uses.

Lignocellulosic biomass is the biological material derived from living organ- isms.It is combination of cellulose, hemicellulose and lignin. It is the primary building block of plant cell walls. It is a complex carbohydrate polymer containing polysaccharides built from sugar mono- mer (xylose and glucose)and lignin, a highly aromatic material. Lignocellulosic biomassincludes woody biomass (forestresidue, wood waste),non woody biomass (agricultural residues like wheat straw, rice straw, barley), bagasse, sorghum, organic waste like animal waste and sewage sludge.The high availability of biomass has ap- peared to be one of the most potential resources. With the availability of such a huge amount of biomass it is believed that this technology is capable of turning negative cost of biomass into positive earning material[5–9].Inner structure of lignocellulosic biomass contributes for the hydrolytic stability. It has resistance to microbial degradation. Cross links are present in the lignocellulosic material between cellulose and hemicellulose with lignin. These cross links are ester and ether linkages. The composition of ligno-cellulosic material is ap- proximately cellulose (30–50%), hemicellulose (20–24%) and lignin (15–35%) composition of lignocellulosic biomass found in different agriculture, industrial masses and wastes is shown in Table 1.

Table 1: *Chemical Composition of Lignocellulosic Materials.*

Lignocellulosic material	**Cellu- lose(%)**	**Hemicellu- lose (%)**	**Lignin (%)**
Hardwood stems	45–50	24–40	18–25
Softwood stems	45–50	25–30	20–30
Leaves	15–20	80–85	0
Wheat straw	30	50	15
Waste from chemical pulps	60–70	10–20	05–10
Grasses	25–30	35–40	15–30
Switch grass	45	31	12

To determine the suitability of nanocellulose production cellulose, hemicellulose and lignin play a key role. For the preparation of nanocellulose a pretreatment is necessary for the separation of cellulose component from the tight bond of polymeric constituents such as; cellulose, hemicellulose and lignin. For increasing the accessibility of cellulosic fiber to chemical attack, mild hydrolysis of isolated cellulose is done by cleaving the ether bond between glucose chains it will produce nano size cellulose intermediate. Fractionation of biomass is a very complex process as the recovery of polysaccharides is required so that all the three components can be fully converted into useful products. Road Map for lignocellulose biomass is shown in Figure 1. It depicts the nanocellulose contents its recovery for valuable products.

LIGNOCELLULOSIC BIOMASS AND ITS RECALCI- TRANCE

Lignocellulosic biomass is the primary building block of plant cells walls. The complex hierarchy structure of lignocellulosic biomass is the main obstacle for key components fractionation where cellu- lose, hemicellulose and lignin are hindered by many physicochemi- cal, structural and compositional factors. The cellulose fiber is itself made up of multilayer's of very small thread like structures called fibrils; these fibrils are exposed by beating of the fibers thereby pro- viding very large area for bonding.The most abundant organic com- pound found is cellulose. Cellulose is the nature's building block found as basic structural material of all trees and plants. Cellulose is found in both crystalline and amorphous forms. Cellulose is long chain polymer with carbon-hydrogen oxygen units. It consists of long chain of D- glucose subunits which are linked by β-1-4 glycosidic bonds. These linear polymers are linked together by different inter and intramolecular bonds, which allow to be packed side by side in planar sheet and bundled into microfibrile. It is high mo- lecular weight, stereo regular and linear polymer of repeating be- ta-D–glucopyranose units. It is the principal structural element and major constituents of the cell wall of trees and plants. The empirical formula is $(C_6H_{10}O_5)_n$ as shown in Figures 2 and 3 where, n is the degrees of polymerization. The main hemicelluloses of softwood are xylans and glucomannan as shown in Figure

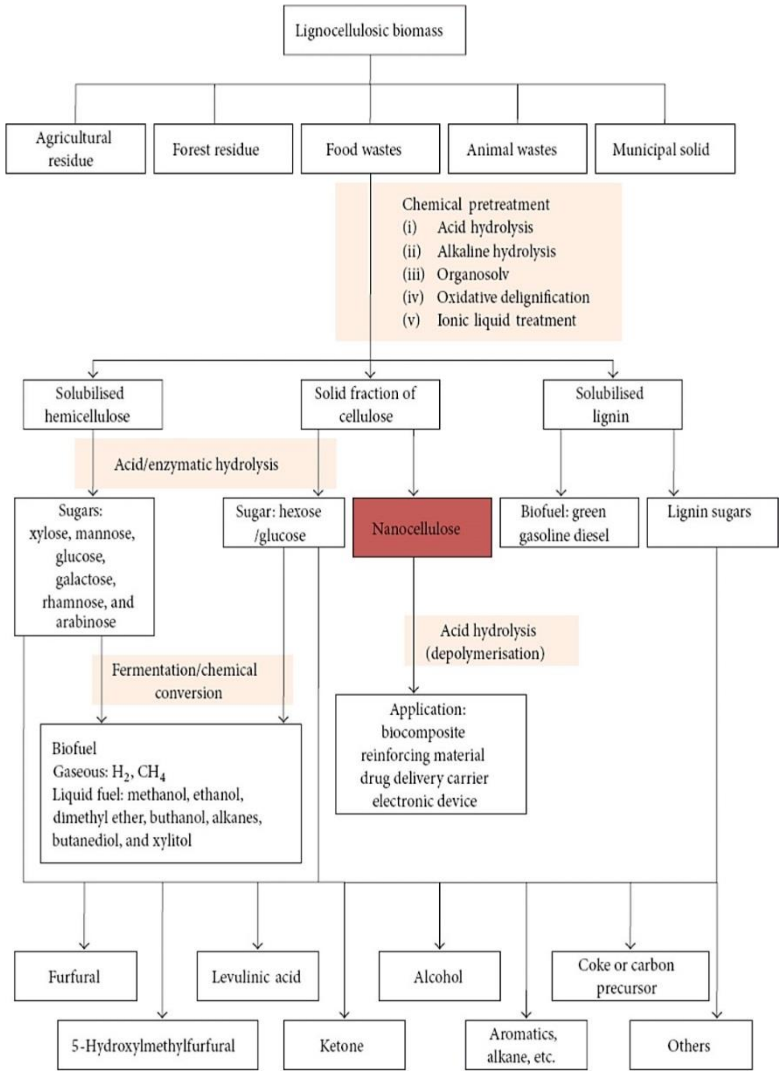

***Fig. 1:** Roadmap of Lignocellulosic Biomass to Nanocellulose Intermediates and Chemicals.*

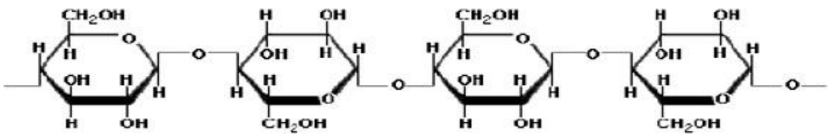

***Fig. 2:**Structure of Cellulose.*

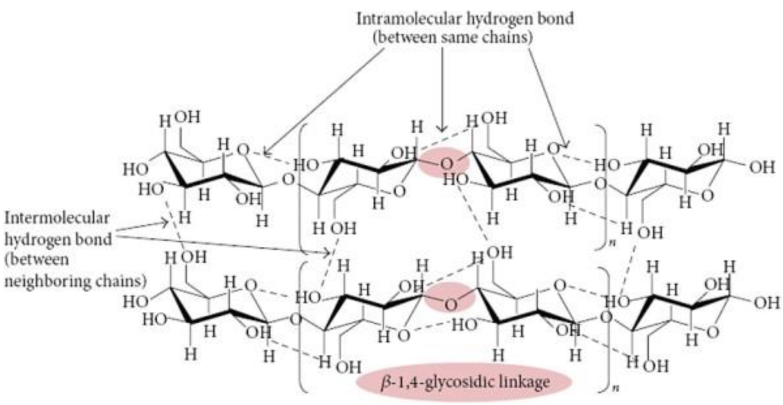

***Fig. 3:**Chemical Structure of Cellulose Chains.*

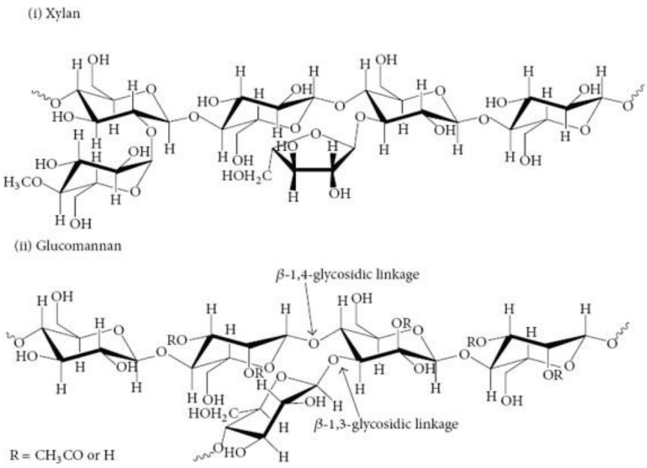

Fig. 4: *Chemical Structure of Hemicellulose Chains.*

Lignin is a complex molecular structure containing cross liked structure containing cross linked polymers especially p-coumaryl alcohol,coniferyl alcoholstructure of lignin is shown in Figure5. Lignin acts as a protective barrier for plant cell wall permeability and resistance against microbial attacks and thus prevents plant cell destruction.Lignin is complex polymers that forma large molecular structure.Lignin gives mechanical strength to wood by gluing the fibers together between cell walls.

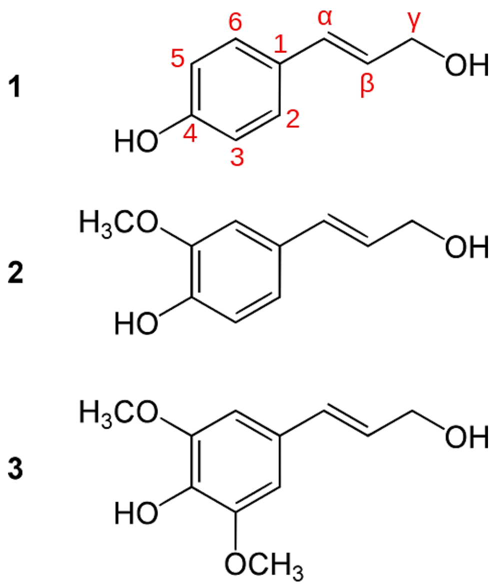

Fig. 5:*Structure of Lignin (1) Para Coumaryl Alcohol (2) Conifer- yl Alcohol (3) Sinapyl Alcohol.*

CHEMICAL PRETREATMENT FOR THE FRACTION- ATION OF LIGNOCELLULOSIC BIOMASS

The pretreatment of biomassis carried out for breaking the ligno- cellulosiccomplex, to solubilise the non cellulosic contents but to preserve the materials for further valorization, reduce cellulose crystallinity and increase the porosity of the materials.An ideal frac- tionation of cellulose from cellulose from lignocellulosic biomass should avoid the structure disruption or loss of cellulose, hemicellulose and lignin content. The supramolecular structure of cellulose should be disrupted, that crystalline domain should be converted into amorphous phases. For this purpose several types of hydroly- sis process by chemical method should be carried out such as; acid hydrolysis, alkaline hydrolysis, delignification via oxidation, or- ganosolv pretreatment and ionic liquid pretreatment (Table 2).

***Table 2:** Functionality, Advantages and Limitations of Chemical Treatment.*

Pre-Treat- ment	Chemical used	Conditions	Mode of Ac- tion	Advantages/Dis- advantages
Conc. Acid		Concen- trated Acid, low temp.	Removal of hemicellulose and lignin	High yields, cor- rosion problems, high demand for chemicals, Environmental problems
Dilute Acid	H_2SO_4	Con. =0.5–2%, T=160ºC	Solublisation of cellulose, direct hyroly- sis of cellu- lose	Low yield, mate- rial loss due to degradation
Ionic liquids		T=150ºC	Solublises the cellulose, degradation of lignin	High cost of sol- vents
Organo- solv	Ethanol- water, Butanol- water, ethylene- glycol	T=150– 200ºC	Extraction of lignin, complete Solublisation of hemicel- lulose	High cost of sol- vents, high energy consumption
Ammoni- arecycled perchlo- ration	Ammonia	T= ~170ºC	Dissolution of lignin	Environmental issues due to am- monia

Acid Hydrolysis

Acid pretreatment is a process to break the rigid structure of ligno- cellulosic material in which hydronium ions breakdown and attack intermolecular bonds among cellulose, hemicellulose and lignin in biomass. Concentrated acids such as;H_2SO_4,HCl,H_3PO_4 and HNO_3 are used to hydrolyse biomass.

Acid hydrolysis helps the biomass deconstruction to maximise monomeric sugars.Long chain structure of cellulose is prefered for nanocellulose. In order to allow disolution of amorphous domains strong acid hydrolysis treatment can be done.The resultant nano particles are called cellulose nano crystals (CNC).

Alkaline Hydrolysis

In alkaline pretreatment lignin structure is disrupted which improve the susceptibility of polysaccharides left. In alkaline hydrolysis the chemicals used are NaOH,KOH,$Ca(OH)_2$,hydrazine and ammonium hydroxide.In the presence of alkali, it serves the functions ofswelling agents to cellulose, leading to increase of internal surface, to decrease in the degree of polym erisationand for crystallinity. Lignin will fail to act as protective sheild to the cellulose after lignin solubilisation.

Ionic Liquids

Ionic liquids pretreatment is pretreatment method for chemi- cal based pretreatment technology. Ionic liquids can dissolve cellulose, hemicellulose and lignin under considerably mild conditions without degrading the chains structure. It is reusable liquids salts at room temperature, typically composed of anions and organic cation.

In biomass degradation isolation of cellulose, pretreatment by ionic liquids could reduce crystallinity of cellulose to amorphous nature. Cellulose in the form of fibrills hydrolyse very less due to inter mo- lecular hydrogen linkages between polysaccharides.

DEPOLYMERISATION OF CELLULOSE TO NANOCEL- LULOSE

Cellulose microfibrile contains crystalline and amorphous regions. Rod like or whisker shaped structuresobtained through acid hydrolysis of wood or plant fibers. These nanoparticles occur as high aspects ratio rod like nano-crystals. Their geometrical dimensions depend on the origin of the cellulose substrate and hyrolysis conditions.

The average length and the width is generally of the order of afew hundreds nanometer. Individual cellulose nanocrystal are produced by breaking down the cellulose fibers and isolating the crystalline regions.

The Acid hydrolysis is the classical way of preparing cellulose nano crystals. However, other processes allowing the release of crystalline domains from cellulosic fibers have been reported, including enzymatic hydrolysis treatment, oxidation, hydrolysis treatment with gaseous acidand treatment with ionic liquids.

Literature shows the importance of cellulose nanocrystal as their strength properties are much higher than those of various metallic and polymeric products. The optical properties of nanocellulose films can be investigated by determining the regular light transmittance with a UV–visible spectrometer.

II. CONCLUSION

In paper industry, nano technological advances are of great importance in targeting high quality, efficiency and market potential. Lignocellulosic biomass is a natural biopolymer with cellulose fibrils in a matrix of lignin and hemi cellulose. One of the most relevant nanomaterials of our paper industry is nano crystalline cellulose, a renewable, recyclable and abundant nano material obtained from lignocellulosic biomass.

Currently the paper industry uses nanotechnology in two ways: to enhance current products and create new ones, and to discover ways that cellulose fibers can be used for prod- ucts outside the industry. In this paper, we have discussed the molecular structure for biomass recalcitrance, reengineering process of lignocellulosic biomass into nanocellulose via chemical approaches.

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