

Sustainable Production of Crystalline-Cellulose from Agric-biomass

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Abstract: Owing to its prolific availability and specific biochemical composition (40-45% cellulose, 25-30% hemicellulose, 20% lignin), Sugarcane bagasse (SCB) attests its potential to cater as perfect starting material for production of value-added compounds namely, furfurals, ethanol, reducing sugars, xylitol, phenolic compounds, zeolites, sorbitol, volatile fatty acids, biogas, etc. Out of which, cellulosic derivatives such as Microcrystalline cellulose (MCC) and Nanocrystalline cellulose (NCC) have been obtained special focus in this study due to their renewable nature and exclusive properties, in particular the high specific surface area, simple functionalization, high thermal stability, low density, high elastic modulus, biodegradability, and biocompatibility. Further, the Crystalline Cellulose Production strategies were assessed for their environmental sustainability using Lifecycle assessment (LCA) approach.

Keywords: Sugarcane bagasse, Microcrystalline, biodegradability, Cellulose.

1. Introduction

Sugarcane is considered as one of the important agricultural crop and sugarcane bagasse, straw are the two kinds of biomass produced in sugarcane cultivation and processing. Sugarcane Bagasse (SCB) residues are produced in huge amounts and which is majorly consumed as a fuel to generate electricity in the industry. SCB is a highly heterogeneous material and composed of about 40-45% cellulose, 25-30% hemicellulose, which consists of mannose, xylose, galactose and arabinose. The remaining

fractions are mostly lignin 18-24% with lesser quantities of mineral, wax (<1%), and ash 1-4%. Cellulose holds substantial applications in the pharmaceutical industry as diluents, lubricants, disintegrates, binders and coatings in the manufacture of tablets and capsule. Production of eco-friendly and high-performance materials has been in the spotlight in recent times, wherein microcrystalline cellulose (MCC) gained prominence for its application in various industries due to its rheological, extruding, physical and mechanical properties. nanocrystalline cellulose (NCC). Nanocrystalline Cellulose (NCC) composed of crystalline nanoparticles made from cellulose, which are highly relevant for the development of new bio-based materials with high commercial value. MCC and NCC production in a simple two-step process was designed and evaluated. Further, these Crystalline Cellulose Production strategies were assessed for their environmental sustainability using Lifecycle assessment (LCA) methodology.

2. Materials and Methods

Sugarcane bagasse (SCB) was collected from M/s. Gayatri Sugars Ltd. Kamareddy, India. SCB was sorted, cleaned and dried in sunlight. The dried SCB was cut into small pieces about 1–2 cm, powdered and the fraction passing 40 mesh size was selected as raw material for the process. Technical grade Nitric acid (HNO₃), Sulfuric acid (H₂SO₄), Hydrogen peroxide (H₂O₂), Sodium hydroxide (NaOH), Acetic acid and Sodium hypochlorite (NaClO) were used. Cellulose microcrystalline, analytical grade was purchased from Sigma-Aldrich as standard for characterization analysis. Environmental sustainability analyses were performed with SimaPro LCA tool. The processed SCB was used as substrate and production of MCC and NCC was achieved by extraction of cellulose from SCB followed by conversion of cellulose to MCC or NCC. The pretreatments were executed with different concentrations of acids, alkali and reaction conditions. Firstly, the ground SCB was mixed with water in 1:10 ratio, autoclaved for 1 h at 15 psi and 121 °C for the removal of hemicellulose fraction. The solution was filtered, and the residue was treated with 10% NaOH at 75 °C for an hour with stirring for the removal of lignin. The solution with lignin was diluted with distilled water to stop the reaction, and was filtered. Then the delignified residue was dried and bleached with 5% CH₃COOH/NaClO at 75 °C for an hour with continuous stirring. The solution thus obtained, was diluted with distilled water and filtered to get cellulose as a residue. Then the cellulose was subjected to

depolymerization in the presence of 30% H_2O_2 and 0.5 mL of conc. H_2SO_4 at 75 °C for an hour. A white turbid solution was obtained through the oxidation process. The solid residue at every step was neutralized to pH 7 by washing with distilled water. The depolymerized cellulose was dried and ground to yield white, crystalline powder.

3. Results and Discussion

3.1 Characterization: The FT-IR spectra, clearly indicates the absorption patterns of the samples at different frequency (wave number) regions (Fig. 1). The characteristic absorption at $3600\text{--}3200\text{ cm}^{-1}$, 2900 cm^{-1} , 1635 cm^{-1} , 1430 cm^{-1} , $1365\text{--}1375\text{ cm}^{-1}$, 1160 cm^{-1} , $1020\text{--}1060\text{ cm}^{-1}$ and 898 cm^{-1} correlating with the standard authorized the presence of cellulosic functional groups in the samples. Absorbance peaks observed in the range of $3400\text{--}3200\text{ cm}^{-1}$ and $2900\text{--}2850\text{ cm}^{-1}$ are associated to stretching of OH groups (alcoholic groups) and aliphatic C–H symmetrical stretching vibration, respectively. The absorbance peaks located near 1635 cm^{-1} , 1375 cm^{-1} and 1060 cm^{-1} are assigned to the O–H bending of absorbed water, in plane C–H bending, and C–C, C–OH, C–H ring as well as side group vibrations respectively. The absorption near 1160 cm^{-1} and 897 cm^{-1} were the characteristic absorptions associated with ether functional groups of C–O–C asymmetrical stretching and C–O–C stretching at $\beta\text{-(1} \rightarrow 4\text{)}$ glycosidic linkages, respectively. Additionally, the spectra absorption peak at 1430 cm^{-1} , which is attributed to a symmetric CH_2 bending vibration and is known as the “crystallinity band” confirms the presence of a greater number of crystalline domains in the samples. In FTIR analysis, the absorption peak of 1735 cm^{-1} , which is specifically assigned to the C=O stretching (Carbonyl group stretching) that represents aldehyde, ketone or carboxylic acids in hemicellulose and the absorption peak near 1512 cm^{-1} , which corresponds to the C=C vibration of aromatic skeletal of lignin are not observed in any of the MCC samples. This ensures the removal of hemicellulose and lignin effectively from bagasse during the pretreatment steps and cellulose only retained in the samples.

The X-ray diffraction demonstrated that all the samples hold the cellulose structure with the fingerprint peaks near 15, 17, 22.5 and 35 2θ values, which was in harmony with the results of FT-IR. Four crystalline peaks have been assumed in the X-ray diffractograms of the current study. Thermal analysis techniques such as TGA, DSC and DTA were assayed to understand the thermal stability parameter of MCC3 with respect to temperature change. TGA curves signified the loss in weight of the sample

with the course of heating with a constant ramp rate. Thermo-gram curve showed two weight loss expressions in the region of 25–600 °C. The first degradation pattern was noticed in the temperature range of 30–120 °C where the loss of weight might be due to the evaporation of surface bound moisture. The inter-molecular hydrogen bonded water present in the sample was evaporated near 120 °C. Maximum degradation was observed from 250 °C to 350 °C, which was about 80% of its total due to the degradation of cellulose by means of decomposition of glycosyl units followed by its transformation to char. Thermal degradation was observed at a lower temperature compared to the cellulose sample within a broader range of temperature manifested the lower thermal stability due to micro size, higher number of free ends in the chain, reduction in molecular weight and degradation of amorphous domains of cellulose. DSC and DTA plot of MCC3 showed two distinct endothermic peaks which relates to the composition of the material. DSC quantified energy flow wherein, first endothermic peak was noticed below 100 °C due to the loss of moisture and second one was observed in between 250 and 400 °C region due to the melting of crystallites, which depicted the nature of decomposition of cellulose. In NCC, the thermal degradation was observed at a lower temperature compared to the cellulose sample within a broader range of temperature manifested the lower thermal stability due to nano size.

3.2 Sustainability Analysis: Life cycle analysis (LCA; ISO 14040:2006) was employed to study the environmental impacts of MCC and NCC production processes with defined system boundaries using SimaPro9.0.0.49 LCA software. The primary data i.e., the data pertaining to the raw materials, chemicals, water, and energy was used as direct input, whereas the secondary data of the processes like production of reactants, nutrients and water was available with the Ecoinvent 3.6 database, provided with the software. The influence of both processes on the major environmental impact categories such as global warming potential, ozone depletion, health factors, resource depletion, and ecotoxicity along with other impacts was evaluated. A gate-to-gate LCA approach was considered in the study to evaluate the respective environmental impacts. The functional unit for the study was set as one-kilogram (kg) of MCC and NCC production, respectively. The lifecycle impact assessment (LCIA) was performed using Impact 2002+ method considering various mid-point impact categories and endpoint impact categories.

The LCA results of both the processes are depicted in Figure 1. The results were clearly displayed the share of each input of the process on

various environmental impact categories, Wherein the electricity consumed in both the processes was evolved to be the prime contributor towards the environmental effects of the processes. In MCC production, Hydrogen peroxide stood as the second significant contributor, majorly influence the carcinogens, mineral extraction, ozone depletion, and respiratory organics. Sodium hydroxide have shown its affect on ozone depletion and mineral extraction.

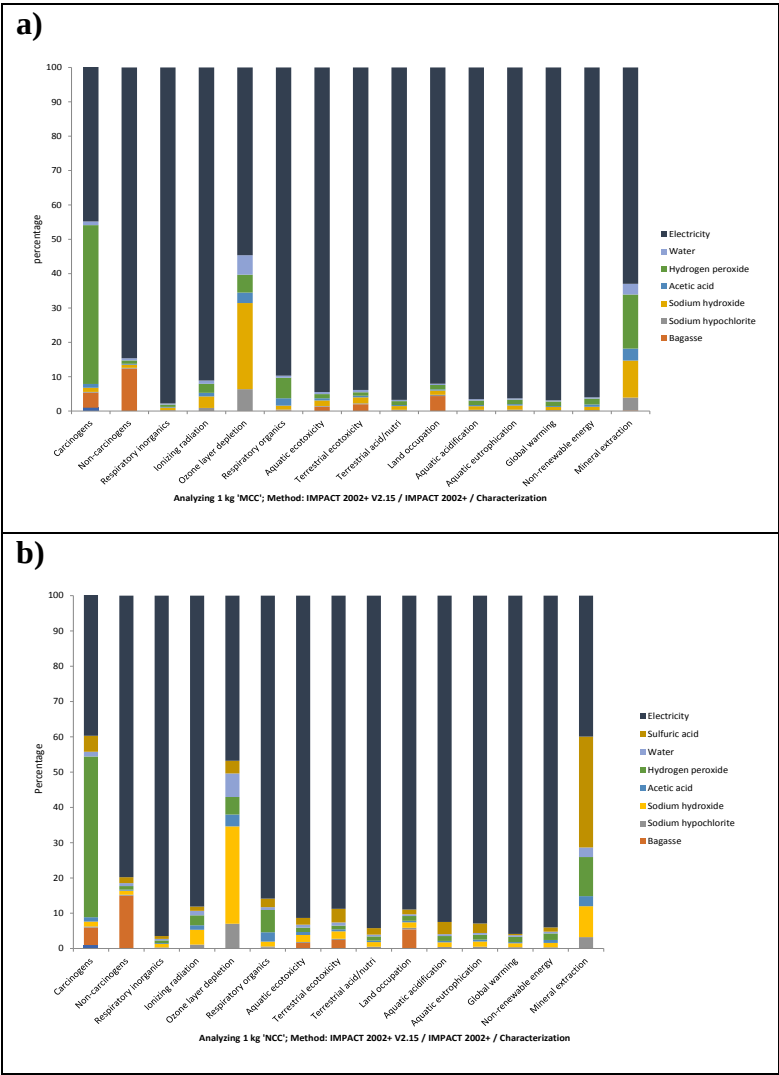


Figure 1. Life cycle Impact Assessment Analysis of (a) MCC production (b) NCC production process using Impact 2002+ LCIA method

On other hand, bagasse has influence on the health (carcinogens and non-carcinogens), terrestrial ecotoxicity, and land occupation. Sodium hypochlorite showed its influence on mineral extraction and ozone layer depletion. On a whole, electricity has shown the highest impact (~95%) on the environment.

Likewise, to the MCC production, electricity was the chief contributor in NCC production process. Although NCC production requires huge amounts of sulfuric acid for the hydrolysis process (Depolymerization), it showed significant impact on mineral extraction category only. Hydrogen peroxide was the second key contributor towards the environment that majorly influence the carcinogens, mineral extraction, ozone depletion, and respiratory organics. The other inputs such as water, bleaching agents have relatively minimum impact on various categories. Sodium hypochlorite showed its influence on mineral extraction and ozone layer depletion. Sankey diagrams prepared with IPCC GWP 100a method are provided in the supplementary material (Fig. 2).

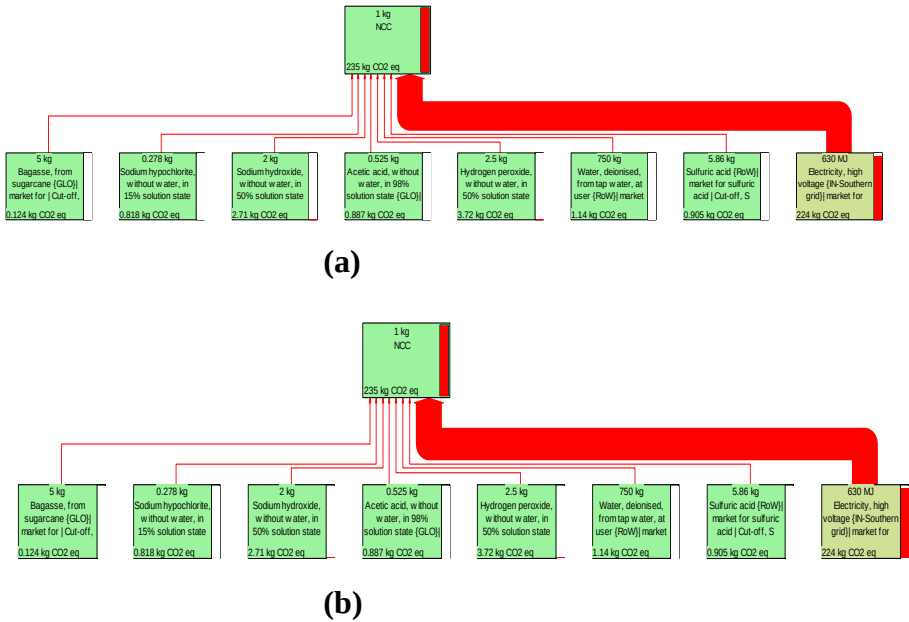


Figure 2. Sankey diagrams of a) MCC and b) NCC production processes using IPCC GWP 100a method

Sankey are special type of flow diagrams, wherein the width of the arrow represents the quantity of the flow and provides a proper understanding on

the contribution of the particular input on the environmental parameters. These diagrams establish a pictorial significance on the major transfers or flows within the system. They are supportive in detecting vital contributions to an overall energy flow in the system boundary. Sankey diagrams of three MCC methods showed more than 95% of the global warming (CO_2 kg eq) contributed by electricity which was main energy input. Electricity utilized in various unit operations was the major contributor towards environmental impact in both the methods. The chemical inputs such as HNO_3 , H_2SO_4 , NaOH , NaClO , CH_3COOH and H_2O_2 showed negligible contribution to the global warming.

4. Conclusion

The study showed an optimized process for production of MCC and NCC using sugarcane bagasse (SCB) as a renewable resource. The produced cellulosic derivatives were characterized with advanced analytical methods like FE-SEM, SEM-EDX, FT-IR, TGA, DTA and DSC analysis, which depicted the significant amendment in the morphology. The utilization of SCB residues as a feedstock for high value derivatives (MCC and NCC) production facilities additional benefits to the existing sugar industries on its entirety use and also drives the growth in bioeconomy.

References

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