CHEMICAL ENGINEERING TRANSACTIONS

VOL. 97, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-96-9; **ISSN** 2283-9216

DOI: 10.3303/CET2297012

Review of The Role of Pretreatment Step in Nanocellulose Production from Rice Straw

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Nanocellulose is one of the most valuable biomass-derived materials, possesses outstanding properties, and is widely used in numerous applications for biomedical fields, packaging, and environmental waste treatment. Rice straw is an abundant by-product from the rice industry and among cellulose-rich feedstocks. The pristine structural network of this raw material is complicated composing cellulose, hemicellulose, and lignin. Therefore, the pretreatment step is necessary to facilitate further stages in the biomass conversion process. The effect of such methods on the characteristics of nanocellulose products from rice straw has not been widely investigated in comparison with other types of biomass. This review summarized the common methods for rice straw pretreatment and the effects of distinct methods on the obtained nanocellulose. Alkaline pretreatment is considered as one of the most effective method for the extraction of cellulose from lignocellulosic complex. Based on a comprehensive summary, this review also shows that cellulose nanocrystals (CNCs) which is usually isolated by acid hydrolysis, has a high crystallinity index due to the removal of amorphous region. Cellulose nanofibrils (CNFs) is obtained by employing mechanical methods to reduce the particle size of cellulose fibers.

1. Introduction

In recent years, biomass feedstocks have been considered to be a renewable source to synthesize a wide variety of profitable materials. The production of lignocellulosic biomass, which is an abundant organic polymer, reached the point of 200 trillion kg/y (Mankar et al., 2021). This indicates that the demand for biomass-based products has been growing sharply. According to the report of Food and Agriculture Organization (FAO), Vietnam is among the five largest rice producers in the world with an annual output of over 40 trillion kg (Minamikawa et al., 2021), meaning that this country possesses an enormous amount of rice straw. The majority of rice straws are currently being burned to generate electricity, compost, or biochar. These processes not only lead to a critical impact on the environment due to the emission of greenhouse gases including CO_2, N_2O, and CH_4 but also do not fully exploit the potential of rice straw materials (Le et al., 2022a). Thus, the utilization of this biomass feedstock for the preparation of more valuable products, such as nanocellulose, is a significant progress in the sustainable development campaign. This contributes to the effort to protect the environment as well as takes full advantage of these by-products from the rice industry.
Rice straw is mainly composed of cellulose, hemicellulose, and lignin which are bound together to form a complex network (Do et al., 2020). Due to the high content of cellulose, rice straw is a common raw material in biogas or bioethanol manufacture, and advanced materials synthesis (Le et al., 2022b). Among these, the production of nanocellulose from rice straw in a facile manner exhibits a huge potential. Generally, nanocellulose (NC) is a natural fiber that has a dimension of less than 100 nm in diameter and several micrometers in length (Nguyen et al., 2021). In fact, nanocellulose can be categorized into three main types including cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and bacterial nanocellulose (BNC) based on the differences

Paper Received: 31 May 2022; Revised: 2 August 2022; Accepted: 1 September 2022
Please cite this article as: Pham C.D., Le T.M., Nguyen C.T.X., Vo N., Do N.H.N., Le K.A., Mai T.P., Le P.T.K., 2022, Review of The Role of Pretreatment Step in Nanocellulose Production from Rice Straw, Chemical Engineering Transactions, 97, 67-72 DOI:10.3303/CET2297012

in particle sizes, crystallinity, and morphology. All these types possess a similar chemical composition (Peng et al., 2011). Besides superior properties of a typical porous material, the existence of numerous hydroxyl groups in nanocellulose networks induces a great affinity towards certain species as well as the opportunity for surface modification, making it a potential candidate in many applications such as food packing (Cuong et al., 2021).
The production of nanocellulose from lignocellulosic feedstock in general and from rice straw, in particular, comprises two stages: The isolation of cellulose from the raw material which is also known as the pretreatment step, and the breakdown of obtained cellulose fibers into the nanoparticles (Pradhan et al., 2022). Although the employment of different pretreatment methods leads to a variety in product properties, the number of researches summarizing the effects of extraction methods from rice straw feedstock is still limited. This mini-review aims to evaluate the effects of the lignocellulosic complex in rice straw on nanocellulose production. The appropriate methods for the extraction of distinct types of nanocellulose were also investigated.

2. Structure of rice straw

Besides the common components of lignocellulosic biomass based-material, rice straw additionally holds a substantial amount of silica due to the polymerization of silicic acid absorbed from the soil. The strong interaction of this compound with cellulose and lignin leads to the difference in the characterization of rice straw in comparison with others (Bhattacharya et al., 2018). Specifically, rice straw is known as one of the most cellulose-rich biomass (more than 45 %) with low content of lignin and hemicellulose (about 20 % each) (Nguyen et al., 2018). Meanwhile, in other types of biomass such as pineapple leaf, although the proportions of lignin and hemicellulose are similar to rice straw, the percentage of cellulose is just over 35. The gummy matter in the plant cell wall of the pineapple leaf is composed of lignin, pectin, and pentosane. This is one of the main influential factors leading to the low efficiency of the biomass conversion process (Song et al., 2021). In other circumstances, coconut coir possesses a high content of cellulose (more than 40%). The lignin quantity is even greater than this number (Sari et al., 2021). Hence, rice straw is an appropriate feedstock for cellulose recovery and the production of nanocellulose, in particular.

3. Extraction of nanocellulose from rice straw

Various approaches are being developed to isolate cellulose from rice straw such as chemical (alkali, dilute acid, or organic solvent), mechanical (ball milling, homogenization), and biochemical methods (enzymatic extraction). Mechanical methods are among the most effective procedures to increase surface area and reduce the particle sizes of lignocellulosic material without the requirement of toxic chemicals. The huge energy consumption and poor productivity in deconstructing biomass networks have hindered the employment of this approach (Harun et al., 2011). Bio-based methods involve both elevated prices and long periods of time during pretreatment. To effectively remove non-cellulosic contents while preserving the materials for further conversion, chemical approaches have emerged as the most appropriate ones due to their efficiency and reasonable cost. There are several typical groups of treatment in this category including acid hydrolysis, alkaline hydrolysis, organosolv, and treatments that utilize oxidation agents or ionic liquids, each of which undergoes a distinct pathway to break down the biomass network (Figure 1) (Lee et al., 2014).

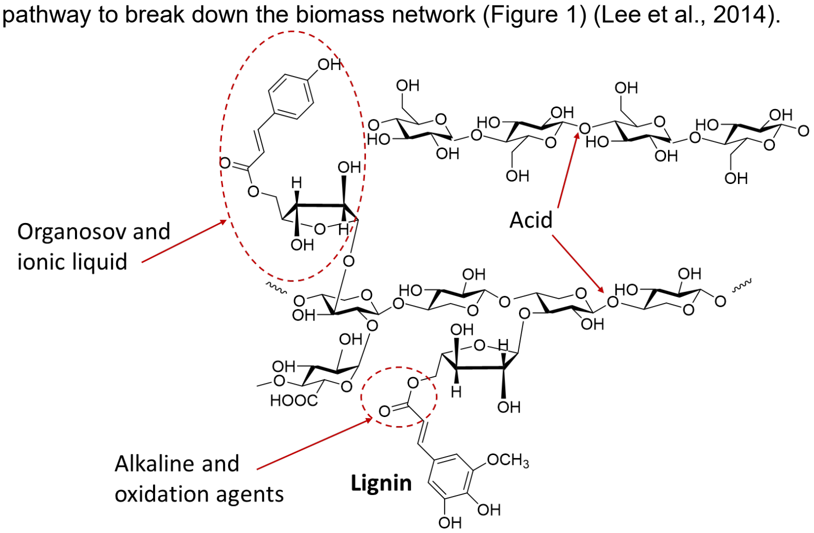

Figure 1: The attack of different agents on the lignocellulosic structure.

3.1 Acid hydrolysis

This treatment involves the attack of hydronium ions from acid molecules to induce the breakdown of intermolecular and intramolecular bonds between cellulose and hemicellulose. The concentration of utilized acids is a decisive factor in determining the severity of the fractioning process. Acids with high concentrations are toxic and corrosive, leading to high capital and maintenance costs (Lee et al., 2014).

3.2 Alkaline and oxidation treatment

The main strategy of alkaline treatment is to separate lignin from the remainder of the biomass structure (cellulose and hemicellulose). This process includes the saponification of the ester bonds crosslinking xylan (hemicellulose) and lignin, leading to the removal of lignin from the original network. The frequently used alkali such as hydroxides and hydrazines also functions as a swelling agent for cellulose, resulting in an increase in internal surface area. Besides, an oxidation agent is also employed in order to remove lignin from the lignocellulose structure. Compounds with oxidative properties such as organic peroxides, ozone, and oxygen have the ability to catalyze the delignification process, resulting in the selective decomposition of lignin and part of hemicellulose in biomass structure (Lee et al., 2014).

3.3 Organosolv treatment and ion liquid utilization

Some studies on extracting CNCs and CNFs are detailed in Table 1 (Lee et al., 2014).

Table 1: Examples of the extraction of nanocellulose from rice straw with different pretreatment methods

Type of NC	Pretreatment	Size modification	Average diameter	Ref
CNC	Dewaxing: Hot water, 1 h Delignification: NaOH 12 wt%, 121 °C, 1 h Bleaching: $NaClO_2$ 5 wt%, 75 °C, 90 mins	H_2SO_4 75 wt%, 30 °C, 5 h followed by sonication.	5–15 nm CrI: 76 % Yield: 90.28 %	(Thakur et al., 2020)
CNC	Dewaxing: Benzene/ethanol [2:1 (v:v)], 90 °C, 12 h Delignification: NaOH 5 wt%, 60 °C, 3 h Bleaching: H_2O_2 and CH_3COOH, 50 °C, 6 h	Ultrasonication -20 kHz, 400 W, 30 mins	10-15 nm CrI: 76.99 %	(Xu et al., 2018)
CNC	Delignification: K_2CO_3-Glycerol deep eutectic solvent, (DES) 140 °C, 60 min, mass ratio 1:9 Bleaching: Oxalic acid-Choline chloride DES, 80 °C, 4 h, molar ratio 1:10	H_2SO_4 64%, 45 °C, 45 mins	12.3-13.3 nm CrI: 76.7 %	(Lim et al., 2021)
CNC	Delignification and bleaching: H_2O_2 30 wt%, 90 °C, 5 h	500 mL ammonium persulfate 1 mol/L, 75 °C, 16 h (for 5 g cellulose fiber)	8-24 nm Yield: 28 %	(Oun et al., 2018)
CNF	_	500 mL ammonium persulfate 1 mol/L, 75 °C, 16 h (for 5 g rice straw fiber)	7–21 nm Yield: 25.6 %	
CNF	Dewaxing: Toluene/ethanol [2:1 (v/v)], 100 °C, 24 h Delignification: KOH 5 wt%, room temperature, 16 h then increase temperature to 90 °C, 2h Bleaching: $NaClO_2$ 1.25 % with a liquid-to-solid ratio of 15 mL/g at 75 °C, 1 h	High-shear homogenization and high intensity ultrasonication	6–20 nm CrI: 65 %	(Dilamian et al., 2019)
CNF	Dewaxing: Ethanol/toluene [2:1 (v/v)], 6 h Delignification: 5 wt% NaOH at 90 °C, 2 h Bleaching: $NaClO_2$ at 70 °C, 1 h	High pressure-grinding at 1500 rpm for 5 times	13.3 nm CrI: 54.4 %	(Zhao et al., 2019)

Organosolv method utilizes volatile organic solvents (methanol. ethanol, ethylene glycol, ethyl acetate, etc.) as a dissolving agent for lignin and several hemicellulosic compounds under heat, resulting in the formation of solid cellulose residue. It was proposed that the hydroxyl groups from the solvents have the ability to promote the cleavage of the bonds between lignin and hemicellulose (acid-ester bonds), leading to the breakdown in biomass structure. In other circumstances, ionic liquids (ILs) are able to simultaneously and effectively dissolve cellulose, hemicellulose, and lignin by homogenizing the reaction medium, making the β-glycosidic bonds become more accessible for catalysts. Certain adjustments are required to alter the selectivity of ILs towards different components in the network and promote the fractionating process.

In general, pretreatment is a crucial step prior to NC production, which is usually divided into 3 stages including dewaxing, delignification, and bleaching. Although the wax content in rice straw is minor, the removal of this component contributes to the increase in conversion process efficiency (Paulraj Gundupalli et al., 2021). The delignification step also plays an important role by removing a substantial amount of lignin, leading to the separation of biomass constituents. And once the crude cellulose is acquired, the bleaching step is necessary to obtain cellulose with extremely high purity (Hassan et al., 2020). As can be seen, the alkaline-utilized method is usually used as one of the most effective ways to disrupt the structure of lignin. In addition, the pretreating solution has the ability to interact with silica in rice straw. Therefore, a substantial amount of non-cellulose compounds was also eliminated from the raw material. This process is carried out under milder conditions, especially when compared with acid pretreatment (Kim et al., 2016). After the cellulose isolation stage, various methods would have been employed to induce the breakdown of cellulose fibers into the nanoscale. Despite having similar chemical compositions, the characteristics of nanocellulose resulted from each breakdown process would vary considerably, depending on the utilized method. Examples for the extraction of different types of nanocellulose would be discussed in the following sections.

3.4 Cellulose nanocrystals (CNCs)

Cellulose nanocrystal is usually isolated from cellulose fibers by acid hydrolysis (i.e., H_2SO_4, HCl) and possesses a high content of cellulose. It usually has a high crystallinity index because of the removal of amorphous zones and extraction of crystalline regions from the raw fibers (Figure 2). Also, due to the breaking of the glycoside bondings in cellulose, nanocellulose obtained from acid hydrolysis method also has a smaller size than other methods (Gan et al., 2020).

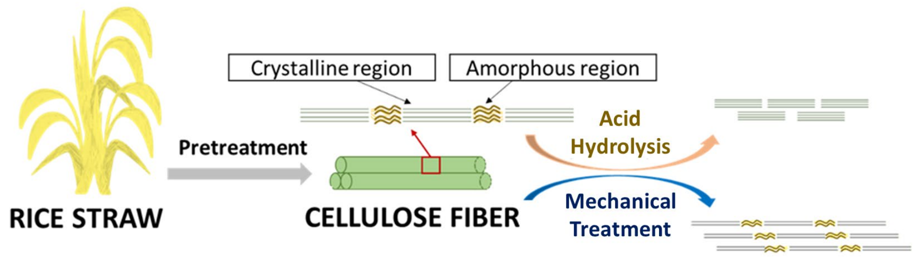

Figure 2: The acid hydrolysis and mechanical treatment of rice straw fibers

In 2020 Thakur (2020), combined concentrated acid with sonification in the production of CNCs. It was revealed that the yield of CNCs production of about 90.28 % was reached when the experiment was carried out at 30 °C for 5 h with H_2SO_4 75 vol%. In other circumstances, Xu (2018) also utilized acid and ultrasonic waves to reduce the particle size of cellulose. The results showed that there was the appearance of rod-like shaped CNCs with the dimension of 10-15 nm in width and several hundred nanometers in length. The crystallinity index increased considerably from the raw material to CNCs due to the removal of lignin and amorphous regions in the structure.

3.5 Cellulose nanofibrils (CNFs)

Despite the similarities in chemical composition when compared with CNC, CNF contains both crystal and amorphous regions in the structure (Figure 2) (Abitbol et al., 2016). To modify the size of the product, mechanical methods were usually used without the requirement of chemicals. This method is easily influenced by a lot of processing factors such as temperature and operating pressure. This process is usually incorporated with other treatment methods to reach a higher extraction yield (Tu and Hallett, 2019).

For example, Dilamian et al. (2019) employed treatments including high-shear homogenization and high-intensity ultrasonication to acquire CNFs. The obtained product has the diameters in the range of 6–20 nm and the crystallinity index increased to 65 % when compared to raw material. In another research, Zhao et al. (2019) investigated the effects of isolation methods on the properties of nanocellulose from rice straw. After being ground at high pressure for 5 times, the CNFs and CNCs from rice straw had the average diameter of 13.3 and 11.4 nm. Also, the results revealed that the CNFs possessed the crystallinity index of 54.4 % and exhibited higher thermal stability when compared with CNCs.

3.6 Bacterial nanocellulose (BNC)

Bacterial nanocellulose is another type of nanocellulose. CNCs and CNFs are extracted from lignocellulose through top-down process. Meanwhile, bacterial nanocellulose is created from the assembly of low-weight sugar molecules known as bottom-up process. BNC has the same chemical composition as two mentioned kinds of nanocellulose, even with a larger surface area per unit. Also, BNC is a hydrophilic material with high purity and contains a substantial amount of absorbed water. It is composed of twisting ribbons which have the diameter in the range of 20-100 nm, and the length of several µm (Kargarzadeh et al., 2017). Though the extraction of BCN does not require former pretreatment to remove lignin or silica from rice straw, the production of BCN has its own drawbacks due to the high cost (Gan et al., 2020). Until now, there is still a lack of studies about the bacterial nanocellulose synthesis from rice straw.

4. Conclusions

With recent achievements in nanomaterials field, this review summarized common methods for the pretreatment step, which is a crucial stage in the preparation of purified cellulose for further conversion. Among various types of biomass, rice straw is considered to be a potential candidate for the production of nanocellulose. It is noteworthy that by varying the conditions in the pretreatment step, synthesized materials exhibited differences in terms of particle sizes, crystallinity, and morphology despite having similar chemical compositions. It was also found the chemical methods, especially alkaline pretreatment have emerged as the most effective approach for the isolation of cellulose from lignocellulosic network. In reality, although the combination of various methods in the production process leads to higher efficiency than the employment of a single one, the production of both CNCs and CNFs comprise multistep and require huge consumption of chemicals and energy. Therefore, in the future, single-step processes carried out under mild conditions need more widely investigation. Furthermore, this work exhibits a solution for utilizing agro-waste in the production of bio-based materials and its great potential in industrial applications.

Acknowledgments

This research is funded by Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number 562-2022-20-04. We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

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