Nanocellulose Preparation from Diverse Plant Feedstocks, Processes, and Chemical Treatments: A Review Emphasizing Non-woods

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Low-cost production of nanocellulose from diverse lignocellulosic feedstocks has become an important topic for developing sustainable nanomaterials. The available feedstocks include both woody and non-woody plants, where the latter are relatively underutilized. Interestingly, the porous structure and low lignin content in most non-woody plants, such as agricultural residues and natural fibers, also makes them ideal sources for lower energy nanocellulose production using simpler methods than those required to process woody plants. To enhance the goal of circularity, this review first provides an overview of the nanocellulose conversion from cellulose and then comprehensively discusses the use of non-woody feedstocks for nanocellulose production. Specifically, the availability of suitable non-woody feedstocks and the use of low-cost processes for pulping and cellulose oxidation treatments, including alkaline, solvent pulping, and nitrogen-oxidation treatments, are discussed. The information in this review can lead to new opportunities to achieve greater sustainability in biobased economies. Additionally, demonstrations of nanocellulose-based water purification technologies using agricultural residues derived remediation materials are highlighted at the end of this review.

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INTRODUCTION

Cellulose is the most abundant polymer in the world, consisting of several hundred to many thousands of connected D-glucose units in the backbone structure, and it is commonly known as an essential compositional element in plants and algae. Recently, the entity of nanocellulose (cross-sectional dimension in between 2 and 10 nm), often considered as the building block of the plant cell wall, has been recognized as a sustainable nanomaterial for many emerging applications. Interest in this material is heightened due to its high surface area, abundant functionalities, and scaffolding capability, while maintaining the unique and environmentally friendly properties of cellulose. Using top-down preparation approaches, two types of nanocellulose can be produced from lignocellulosic feedstocks: cellulose nanofibers (CNF) and cellulose nanocrystals (CNC). CNFs are longer, pliable, and less crystalline, and they can intertwine among themselves. Alternatively, CNCs are shorter, rigid, with higher crystallinity. CNCs often appear as rodshaped nanoparticles with lower aspect ratios. The choice between CNF and CNC depends on the requirements of the targeted application. Additionally, bacterial nanocellulose (BNC) can be produced by bacteria using sugar solutions as feedstocks through the bottom-up approach. The details of structures and properties in these different nanocelluloses have been comprehensively discussed in recent reviews (*e.g*., Das *et al*. 2022; Lv *et al.* 2023).

In a chosen defibrillation process, the choice of feedstock can play a vital role in determining the required consumptions of energy, chemicals, and water to produce nanocellulose. Typically, non-woody materials with looser structure need less energy (and chemical treatments) for nanocellulose production, where relatively simple pulping/ defibrillation methods can be adopted. Often these materials, such as agricultural residues and natural fibers, are considered less valuable than woody materials for conventional applications in construction and packaging. As a result, these non-woody biomasses, although truly abundant, are relatively underutilized around the globe. For example, China currently produces over 56 million tons of agricultural waste per annum (Kamel *et al*. 2020), and the United States is projected to produce 320 million tons of primary crop residues by 2030, including corn stover, wheat straw, barley, sorghum, and oats residues. (US-DOE 2011). Such residues are commonly used either as soil amendments, animal feeds, or for biofuel production. In the last decades, there have been extensive efforts to explore the usage of non-woody fiber residues for ethanol production. However, these efforts have been gravely challenged by the low oil prices; thus, the economics are simply not viable. Several research groups have also investigated the concept of integrated production of nanocellulose and biofuel, but the economics are still not clear (Menon and Rao 2012; Zhu *et al.* 2011). As agricultural residues are truly abundant and low-cost, and their improper disposal can also cause grave environmental consequences, there is an urgent need to explore simple ways to upcycle these materials and create new economic opportunities.

Agronomic benefits of agricultural residues and natural fibers over woody materials vary from species to species, where the most visible benefits of these non-woody plants include shorter growth cycles and higher biomass yield. Some non-woody plants, such as jute and sorghum, also exhibit lower recalcitrance for biorefinery than wood due to their relatively low lignin content. In other words, these plants require less energy to remove lignin and hemicellulose components, which is the primary step for nanocellulose production. There are, however, other factors that must be considered for valorization of non-woody feedstocks, such as collection, transportation, decortication, drying process, and retting, which are all essential economic and technological issues for agro-based and non-woody fiber manufacturing. Firstly, as the handling, storage and preparation of these materials have not received the same attention as that for woody materials, one must consider their potentially serious logistical problems. For example, the long-distance cost to transport agricultural residues can be prohibitively high. Thus, in large-scale production of fruits, such as palm oil fruit, citrus, and coconut, it may be a viable approach to process the waste on site, to reduce costly transportation logistics. Secondly, the morphology and chemical composition of non-woody plants and their specific breed often depends on harvesting time and geographic location. Thus, their pulp properties change seasonally. This variability of fiber properties constitutes a major challenge to runnability and efficiency of continuous large operations. To continue, the handling of agricultural residues and natural fibers is often labor-intensive, especially for leaf and fruit fibers, due to hand-stripping, while natural fibers require decorticating equipment, which is commonly used for many stem-fiber crops. Moisture content control and storage conditions are also critical factors, with an extensive number of books and papers dealing with such issues (Young, 1997a,b). Thirdly, most non-woody plants contain silicate compounds, which may remain with the fibers in acidic processes, but dissolve in alkali, which will complicate the recovery operations, while high ash content which is particularly prevalent in the family of grasses (Poaceae), poses its own set of challenges. In summary, the handling, preparation, storage, and transportation logistics of utilizing agricultural residues, including the variability of the feedstock and the issue of the high ash content in some of these materials, can create difficulties for large scale modern facilities (such as greenfield kraft pulp mills), and require substantial investment cost and a large minimum production capacity (usually in the range of 500 to 1000 kton/year) for economical operation. Hence, the challenge is to find a suitable and economically feasible treatment method to process non-woody materials, such as agricultural resides and natural fibers, which will be discussed in detail in this review.

The major aim of this review is to improve the circularity of bioeconomy by converting low-valued non-woody feedstocks to high-valued nanocellulose. However, considering the diverse interests of potential readers, the first part of this review summarizes the conversion of non-woody lignocellulosic biomass into nanocellulose using different production methods along with the introduction of some essential subjects related to the field. After that, this review contains an overview of agricultural residues and natural fibers, focusing on (i) the availability of these non-woody feedstocks to produce high quality nanocellulose, especially CNF, (ii) the composition of various biomasses, and (iii) low-cost processes that have been demonstrated for the manufacture of nanocellulose and the viability of their upscaling. Various pulping processes, their advantages and disadvantages, and the development of a unique *zero-waste* nitro-oxidation process (NOP) are reviewed and discussed. Perspectives on the use of small mills for possible adoption of some of these technologies are also discussed. As there is not yet a market for nanocellulose in the order of million tons/year due to its relatively high cost, this article also argues that the development of viable nanocellulose manufacturing facilities using agricultural residues (or agro-waste) should be small-scale operations, unless operated as a biorefinery.

Conversion of Cellulose into Nanocelluloses

In the past few decades, a plethora of methods have been demonstrated to prepare nanocellulose from lignocellulosic plants (Table 1) and bacterial materials. Many publications and reviews have covered these methods and the corresponding structure-property relationships in resulting nanocellulose. These methods include chemical treatments, biological treatments, and mechanical treatments. This section will summarize some highlights of these methods and the distinct physicochemical properties of resulting nanomaterials.

Chemical treatments

Methods using suitable chemical treatments to attain nanocellulose from lignocellulosic feedstocks can vary depending on the starting feedstocks as they contain different contents of cellulose, lignin, hemicellulose, pectin, and other organic compounds. Typically, a pretreatment method can be used to remove the non-desired hetero-polymers and organic substances (Habibi 2014). The lignin component can be removed using both acid and bases. However, the efficiency of the removal and the type of lignin removed may vary depending on the concentration of acid and base, types of acids and bases, temperature, additive used, size of the starting material, the amount present, and the composition of both biomass and lignin (Klemm *et al.* 2011; Baruah *et al.* 2018; Mankar *et al.* 2021).

Table 1. Acidic Hydrolysis Treatments of Agricultural Residues and Natural Fibers for Nanocellulose Production with Diverse Structural Dimensions

Feedstock	Method	Nano-cellulose Type	Diameter (nm)	Length (nm)	Crystallinity (%)	Reference
Bamboo	Sodium hydroxide, sulfuric acid	CNC		200	71.98	(Yu *et al.* 2012)
	Sodium hydroxide, sulfuric acid, acetic acid	CNC	10	-	70.3	(Do *et al.* 2023)
	Sodium hydroxide, hydrochloric acid	CNF	69.97	959.45	68.51	(Lin *et al.* 2022)
Banana	Sodium hydroxide, sulfuric acid	CNC	16.35	181.65	64.12	(Mishra *et al.* 2022)
	Sodium hydroxide, sodium chlorite	CNF	10-53	**-**	54.5	(Franco *et al.* 2019)
Sugarcane	Sodium hydroxide, hydrochloric acid	CNF	57.7	364.84	58.32	(Gond *et al.* 2021)
	Sodium hydroxide, sulfuric acid	CNF	35	175	-	(Mandal & Chakrabarty 2011)
Palm	Sodium hydroxide, sulfuric acid	CNF	-	108	73	(Mehanny *et al.* 2021)
Wheat	α-Amylase sodium hydroxide	CNC	33.8	644.77	88	(Xiao *et al.* 2019)
Jute	Sodium hydroxide, oxalic acid, steam explosion	CNF	50	-	62.54	(Thomas *et al.* 2015)
Cotton	Sulfuric acid	CNF	-	179.3	91	(Morais *et al.* 2013)
	Hydrochloric acid, TEPMO	CNC	6.5	207	78.2	(Jordan *et al.* 2019)

Acid and base treatments of the biomass can also reduce the cellulose component to a lower degree of polymerization, since both acid and base can hydrolyze the glycosidic bond of the cellulose chains. Other chemical pretreatments include the use of organic solvent mixtures, ammonia fiber explosion, co-solvent enhanced lignocellulosic fractionation, supercritical fluids, deep eutectic solvents, and TEMPO-oxidation (Mankar *et al.* 2021) The most common industrial pretreatment process is kraft pulping, using a mixture of sodium sulfide and sodium hydroxide to produce nearly pure cellulose. The details of these chemical treatments are extensively discussed in the later parts of this review.

Pretreated cellulose materials can be further chemically treated to produce nanocellulose. For example, acid hydrolysis (using hydrochloric acid or sulfuric acid at relatively high concentrations) of pretreated cellulose materials can remove residual lignin and hemicellulose as well as some amorphous cellulose and yield highly crystalline CNC, which have also been called cellulose "whiskers". CNC has a rod-like shape with a diverse range of cross-sectional dimensions between 5 and 70 nm and a length typically around 100 nm (Cheng *et al.* 2017; Kusmono *et al.* 2020; Pawcenis *et al.* 2022; Wulandari *et al.* 2016; Yu *et al*. 2013). Table 1 summarizes the effects of some common acid treatments on the structure of CNF and CNC using different biomass feedstocks.

In addition to acid hydrolysis using relatively strong acids, some chemical methods using milder conditions also have been demonstrated. For example, Ji *et al.* (2019) demonstrated a relatively green method using citric acid (60 to 80%) for 0.5 to 4 h, followed by 20 min of sonication to produce both CNC and CNF from bleached sugarcane bagasse. The nanocellulose products created by this method included CNC with a cross-sectional dimension between 20 and 30 nm and a length between 250 and 450 nm, as well as CNF with a larger cross-sectional dimension between 30 and 60 nm and a length between 500 and 1000 nm (Ji *et al.* 2019).

Another popular chemical treatment for nanocellulose production is TEMPO-mediated oxidation of cellulose *via* the use of the 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO) agent, sodium bromide, and sodium hypochlorite at pH = 10. The crystallinity, degree of polymerization, degree of oxidation, and aspect ratio of the resulting cellulose nanoscale fibers can be controlled by varying the amount of sodium hypochlorite and the number of homogenization cycles (Zhou *et al*. 2018). The creation of carboxylate groups due to TEMPO reaction can lead to anionic charges on the cellulose surface, which can facilitate the defibrillation process, leading to a small cross-sectional dimension between 5 and 10 nm and a length between 100 nm and a few micrometers, depending on the experimental conditions (Saito *et al*. 2007). In the TEMPO reaction, the radical TEMPO-catalyst is first oxidized by sodium hypochlorite to generate the N-oxoammonium-type structure, where the oxoammonium compound can subsequently oxidize the cellulose surface (Isogai *et al.* 2018).

There are other radical reaction methods used to produce nanocellulose from cellulose pulps. For example, in the Fenton-oxidation approach, a transitional metal with a low oxidation state can be used to react with hydrogen peroxide and generate hydroxyl radicals (Shokri and Fard 2022). In such a reaction, iron is the most common type of metal employed, as it is naturally abundant and possesses the oxidation state of +2 and +3. Fan *et al.* (2019) demonstrated that microcrystalline cellulose can be converted into CNC using 30% H_2O_2 and $FeSO_4$ at 60°C. The resulting nanocellulose had a cross-sectional dimension between 19 and 23 nm, a length between 92 and140 nm, and the degree of carboxylation as high as 2.2 mmol/g.

While Fenton oxidation uses metal to catalyze the generation of hydroxyl radicals, oxidants such as ammonium persulfate (APS) can also break down and create highly reactive sulfate radicals at moderately elevated temperatures (60 to 80 °C). These sulfate radicals are capable of simultaneously pulping and oxidizing cellulose (Leung *et al*. 2011) In one study, when *Sansevieria trifasciata*, commonly known as "snake plant" or "in-law's tongue", was treated with 1.5 M APS at 70 °C for 16 h, the reaction resulted in nanocellulose with an average width of 7.4 ± 2.7 nm, an average length of 156.4 ± 54.6 nm, and a crystallinity index of 87.4% (Indirasetyo and Kusmono 2022). Another study showed that the use of N,N,N',N'-tetramethylethylenediamine along with APS could increase the yield of carboxylated CNC (up to 62.5%) for cotton pulp, where the crystallinity index could rise to 93% (Liu *et al.* 2020).

Ionic liquids are different classes of salts that consist of cations and anions, and they exist in the liquid state at room temperature. Certain ionic liquids can dissolve cellulose and hydrolyze cellulose. Haron *et al.* (2021) published a review on the use and effects of different ionic liquids for nanocellulose production. Their properties and efficiencies and sustainability issues were highlighted. With the appropriate usage, ionic liquid can be used to produce nanocellulose from cellulose, while recycled ionic liquids can be used multiple times without losing much of their efficiency. For nanocellulose production, some demonstrated ionic liquids have included [Bmim][Cl] (1-butyl-3-methylimidazolium chloride) [Bmim] [OAc] (1-butyl-3-methylimidazolium acetate), [Bmim] [HSO_4] (1-butyl-3-methylimidazolium hydrogen sulfate), [Emim][Cl] (1-Ethyl-3-methylimidazolium chloride), and [Emim][OAc] (1-ethyl-3-methylimidazolium acetate). The nanocellulose treated with ionic liquids typically exhbited a cross-sectional dimension between 15 and 20 nm (Haron *et al.* 2021).

Work in the authors' lab demonstrated that when raw lignocellulosic feedstock (*e.g.*, untreated jute biomass) was treated with a mixture of nitric acid and sodium nitrite, both pulping and cellulose oxidization processes could simultaneously occur. This reaction is termed the nitro-oxidation process, and it is capable of producing carboxylated nanocellulose from any lignocellulosic feedstock. The resulting nanocellulose typically possesses an average cross-sectional dimension of about 5 nm and a length ranging from 200 to 2500 nm (Sharma *et al*. 2018b,c).

Biological treatments

Biological treatments using fungi or enzymes to remove lignin and hemicellulose from lignocellulosic biomass are often viewed as environmentally friendly and inexpensive methods to produce nearly pure cellulose. Notably, biological treatments require significantly less energy than that of mechanical treatments. The most common biological pretreatment to remove lignin and hemicellulose from raw feedstock is with fungi. Two types of fungi are typically used – hydrolytic and lignolytic. Hydrolytic microorganisms are responsible for degradation of polysaccharides (*i.e.*, cellulose and hemicellulose), whereas lignolytic microorganisms are responsible for degrading lignin. For pulping purposes, white-rot, brown-rot, and soft-rot fungi are typical classes of microorganisms utilized. In the case of enzymes, species such as laccases, lignin peroxidase, manganese peroxidase, and versatile peroxidase are also efficient in removing lignin. Extensive discussions of biological pretreatment have been made by Baruah *et al.* (2018) and Østby *et al*. (2020). Once the pure cellulose is produced, various enzyme strains can be further used to produce different-sized cellulose. The final product, purity, aspect ratio, and water content can be finely tuned by using different strains of bacteria and pH medium. Some notable examples are as follows.

Lytic polysaccharide monooxygenases (LPMOs) are mononuclear copper enzymes that can cleave the glycosidic bond of cellulose by inserting oxygen at the C1 and/or C4 positions and oxidizing the reducing end. It has been demonstrated that the addition of LPMO in pretreated flax pulps, cotton linters, softwood (birch), and hardwood pulps could directly produce CNC and CNF (Karnaouri *et al.* 2022). Endoglucanase enzyme was also found to be able to hydrolyze the glycosidic bond in cellulose, especially in the amorphous region, and when added to pretreated flax and hemp fibers, endoglucanase enzyme can yield rod-like nanofibrils with cross-sectional dimension of about 10 nm and length about

200 nm (Xu *et al.* 2013; Wang *et al.* 2016). Many commercially available enzymes are used in combination with chemical and/or mechanical treatments to produce CNC and CNF from agricultural residues. Some examples include Fibercare® enzyme for treating wheat straw, curauá fibers, and bleached eucalyptus kraft pulp; Pectinase PL Amano™ enzyme for treating orange peel; Optimash™ VR enzyme for treating soybean straw; and cellulase enzyme (from Sigma) for treating bagasse pulp (Michelin *et al.* 2020). While enzymatic hydrolysis can generally produce nanoscale fibers with good transparency and high specific surface area, for large-scale operations, mechanical treatments are often supplemented for nanocellulose production (Aguado *et al.* 2022).

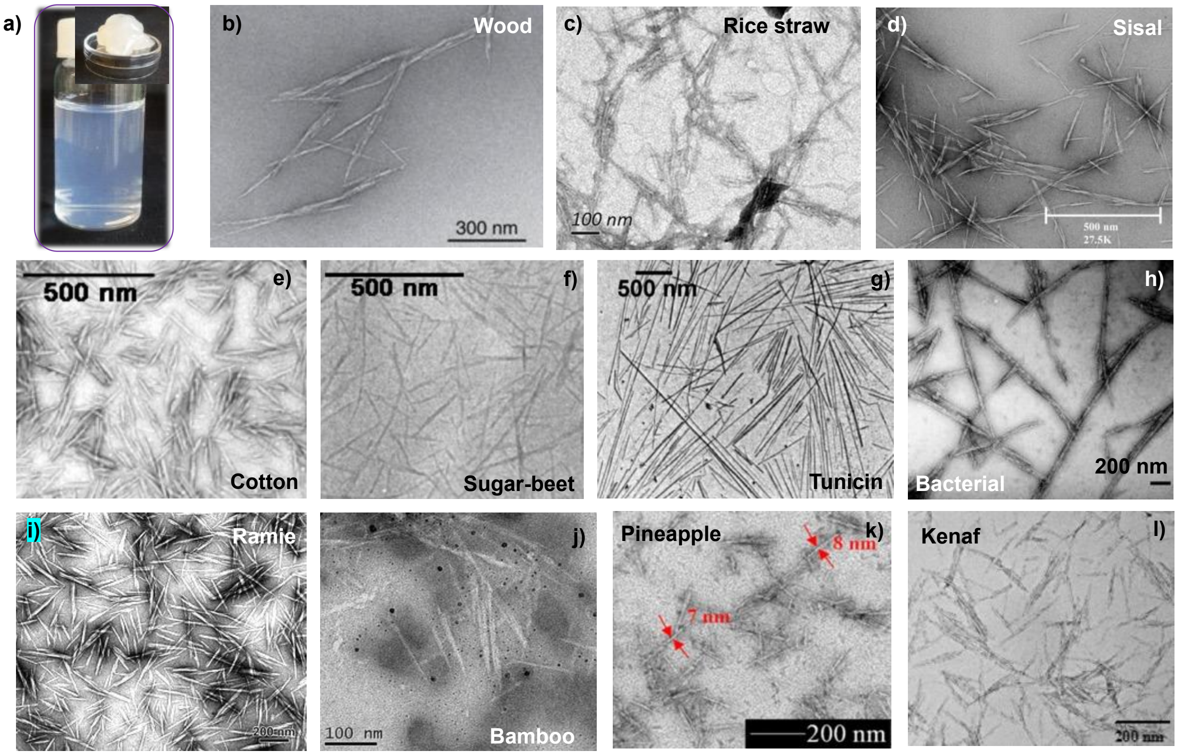

Fig. 1. TEM images of CNCs prepared from different feedstocks using different treatment conditions. These images show some structural variations but similar CNC characteristics. (a) Photographs of sulfuric acid hydrolyzed CNCs suspension (1.0 wt%) (inset: a 10.0 wt% CNC hydrogel), and (b) corresponding TEM image of CNC derived from wood pulp. (c)-(l) TEM images of CNCs derived from different feedstocks using different treatment conditions (Azizi Samir *et al*. 2005 [Reprinted with permission from *Biomacromolecules* 6(2), 612-626, American Chemical Society]; Cheng *et al*. 2022 [Permission from SpringerNature, Reprinted from "Comparative study on properties of nanocellulose derived from sustainable biomass resources," *Cellulose* 29(13)]; Habibi *et al*. 2008 [Used with permission of Royal Society of Chemistry from "Bionanocomposites based on poly (ε-caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization," *Journal of Materials Chemistry* 18(41)]; Lin *et al.* 2022 [Reprinted from *Front. Chem.* 10:922437, CC BY]; Pornbencha *et al.* 2023 [Reprinted from RSC, CC BY-NC 3.0 Deed]; Roman and Winter 2004 [Reprinted with permission from *Biomacromolecules* 5(5), 1671-1677, ACS]; Siqueira *et al.* 2010 [Reprinted with permission from *Langmuir* 26(1), 402-411, ACS]; Usov *et al.* 2015 [Reprinted from *Nature Communications* 6, 7564, CCBY]; Zainuddin *et al.* 2017 [Used with permission of Elsevier from *Carbohydrate Polymers* 163, 261-269]; Zhao *et al.* 2019 [Used with permission of SpringerNature, CC-BY-NC-ND).

Mechanical treatments

Mechanical treatments are frequently used to pulverize raw biomass such as agricultural residues before and after the applications of other physical or chemical procedures to produce nanocellulose. Common mechanical treatments include grinding, milling, extrusion, high-pressure homogenization, cryocrushing, and sonication. The descriptions of different mechanical methods for nanocellulose production can be found in several reviews (Habibi 2014; Islam *et al*. 2014; Jonoobi *et al.* 2015; Patil *et al.* 2022; Sanchez-Salvador *et al.* 2022a). While mechanical treatments alone cannot generate pristine nanocellulose from raw biomass, they can be used in tandem with other chemical or enzymatic treatments to increase the yield and crystallinity of nanocellulose, which will be discussed later. However, mechanical treatments require additional cost due to the energy consumption that varies with the structure of the feedstock. Therefore, one should carefully select an appropriate biomass feedstock for producing cost-effective nanocellulose for practical applications.

Serra-Parareda *et al*. (2021) reported that the nature of raw feedstocks can also impact the resulting nanocellulose structure and morphology. Transmission electron microscopy (TEM) images of CNC and CNF derived from various feedstocks using different treatment methods are illustrated in Figs. 1 and 2, respectively. From these images it is apparent that the size and shape of nanocellulose are very different due to the variations in feedstock materials and treatment conditions.

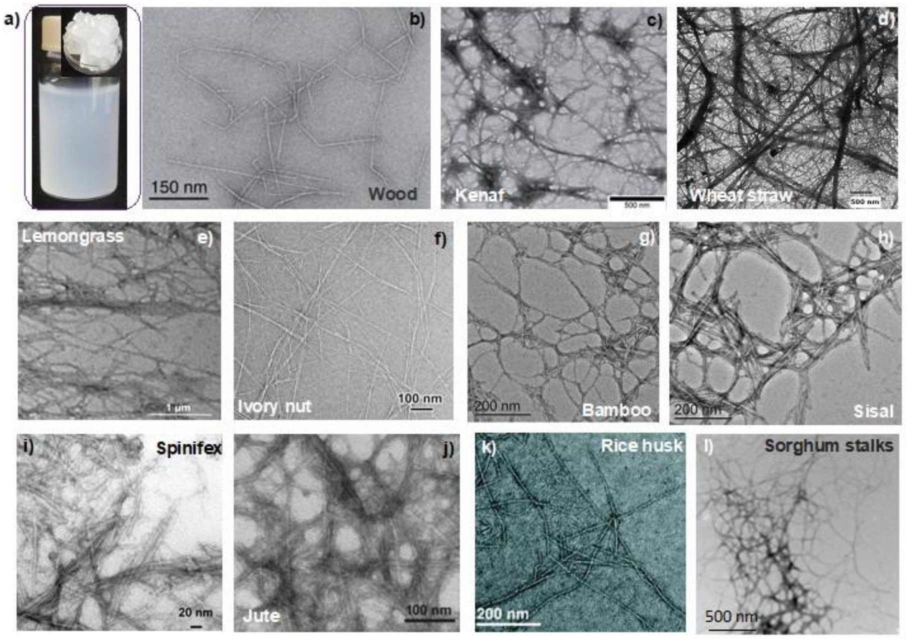

Fig. 2. TEM images of CNFs prepared from different feedstocks using different treatment conditions. The images show some structural differences but similar CNF characteristics. (a) Photographs of TEMPO oxidized 2.0 wt% CNF suspension (inset: 10.0 wt% CNF hydrogel) and (b) corresponding TEM image of CNF derived from bleached softwood kraft pulp. (c)-(l) TEM images of CNFs derived from different feedstocks using different treatment conditions (Alemdar and Sain 2008 [Reprinted with permission of Elsevier]; Usov *et al.* 2015 [Reprinted from *Nature Communications* 6, 7564, CCBY]; Sharma *et al.* 2017b, 2018a [Reprinted from *Biomacromolecules*, Copyright 2017, American Chemical Society, and *ACS Sustainable Chemistry and Engineering*, Copyright 2018, ACS]; Chen *et al.* 2019 [With permission from SpringerNature, CC-BY-NC-ND]; Chen *et al.* 2022 [Reprinted from *Nanomaterials*, CC BY]; Kumari *et al.* 2019 [With permission from SpringerNature, CC-BY-NC-ND]; Narkpiban *et al.* 2019; Zhan *et al.* 2020 [Used with permission of RSC, from *Water Research* & *Technology* 6(11), 3080-3090]; Carvajal-Barriga *et al.* 2022, CC BY, Permission granted by authors).

Although the combination of the microscopic technique (*e.g.*, TEM) and image analysis tool can provide information about the nanofiber width, it is relatively difficult to determine the nanofiber length because of the fiber entanglement and the vague existence of nanofiber ends. Furthermore, as the CNF suspension becomes inhomogeneous, the images can contain both individual and aggregates (bundles) of nanofibers. In this case, the fiber width can vary along the fiber length, unless they are sufficiently delaminated (Balea *et al*. 2020). In this regard, CNC materials are relatively easier to characterize. In their review, Balea *et al.* (2021) examined the challenges related to nanocellulose characterization and attempted to address the question of why the market has yet to realize its full potential.

Overview of Agricultural Residues and Natural Fibers for Nanocellulose Production

There have been extensive investigations of nanocellulose production from agricultural residues and natural non-woody fibers. As shown in Fig. 3, a great deal of publications can be found that focus on the characterizations and applications of CNCs and CNFs derived from non-woody feedstocks (including algae). Unfortunately, the amount of published work does not correlate with their economic viability. Because of the relatively high crystallinity (typically around 50%), large surface area (nearly 100 m^2/g) and effective fiber network formation capability (Rocha *et al*. 2018), CNF has secured its position as emerging sustainable nanomaterials for electronic and biomedical applications (amounts to 31% and 29% of the total publications, respectively).

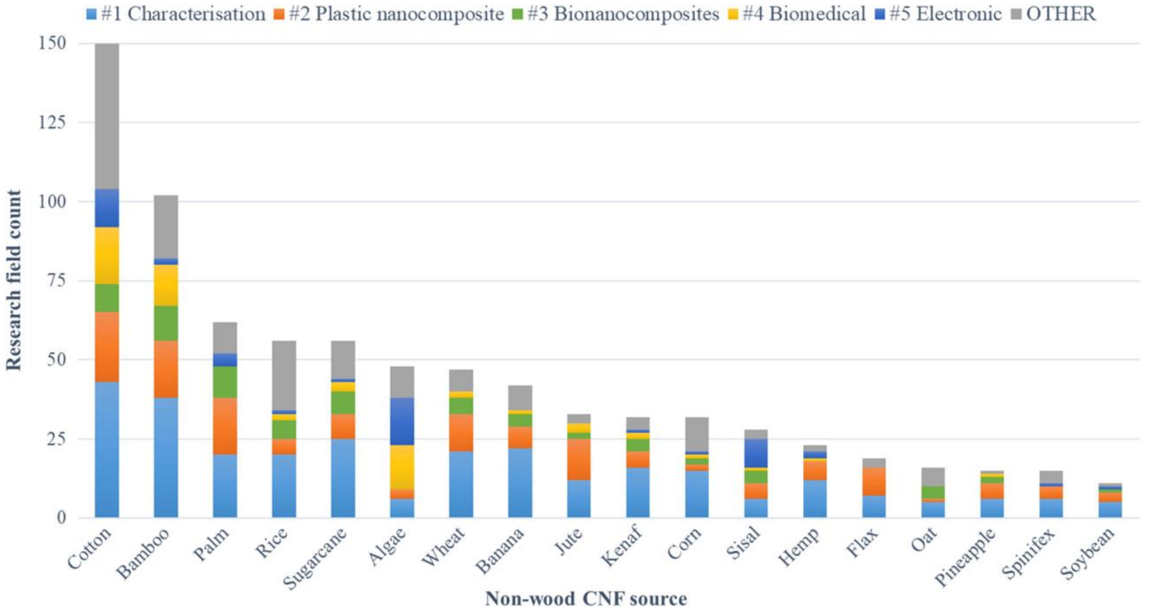

Fig. 3. Top CNF research fields for top 18 non-woody biomass feedstocks (Pennells *et al.* 2020, with permission from SpringerNature, CC-BY-NC-ND)

In Table 2, the chemical composition (*i.e.*, cellulose, hemicellulose, and lignin) and annual production yield of some agricultural residues are tabulated. In Table 3 the data are also summarized for natural plant fibers and some agricultural fibers, from which nanocellulose can be extracted, albeit not at commercial scale to our knowledge.

Table 2. Chemical Compositions and Annual Production Yields of Varying Agricultural Residues (Tye *et al.* 2016)

Agricultural Residue Type	Source per Annum (M. tons)	Type of Non-Woody Biomass (M. tons)	Agricultural Residue (M. tons)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Barley	141.4	Barley straw	51.3	33.3-42	20.4-28.0	17.1
Corn	962.4	Corn stover/straw	376.8	35.0-42.6	17.0-35.0	7-21
Oat	22.9	Oat straw	10.4	37.6	23.3	12.9
Rice	473.1	Rice straw	65-75	32.0-47.0	18.0-28.0	5.5-24.0
Sorghum	61.9	Sorghum straw	12.0	32.4	27.0	7.0
Wheat	705.6	Wheat straw	472.2	33.0-45.0	20.0-32.0	8.0-20.0
Sugarcane	1741.3	Sugarcane bagasse	1044.8	45.4	28.7	23.4
Oil palm	277.7	Empty fruit bunches	63.9	35.8-56.0	21.9-44.0	15.1-17.9
		Mesocarp	40.3	19.0	15.2	30.5
		Shell	18.0	14.7	16.4	53.6
		Frond	72.9	31.0	17.1	22.9
		Trunk	19.4	39.9	21.2	22.6

Table 3. Chemical Compositions and Annual Production Yields of Varying Natural Plant Fibers (mainly from non-woody plants)

Lignocellulosic Plant	Fiber Annual Production (M. tons)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Grass					
Bamboo	30	42	27	23	(Chen *et al*. 2011a; Faruk *et al.* 2012)
Spinifex	-	33	44	23	(Amiralian et al. 2015)
Coastal bermudagrass	200.0	25.0	35.7	6.4	(Tye *et al*. 2016)
Miscanthus	256.4	40.0	18.0	25.0	(Tye *et al*. 2016)
Switchgrass	282.9	30.0-50.9	10.0-40.0	5.0-20.0	(Tye *et al*. 2016)
Bast fiber					
Flax	0.5	60.0-81.0	18.6-21.0	2.2-12.0	(Tye *et al*. 2016)
Hemp	0.1	70.0-92.0	18.0-22.0	3.0-5.0	(Tye *et al*. 2016)
Jute	2.5	51.0-84.0	12.0-20.0	5.0-13.0	(Tye *et al*. 2016)
Ramie	0.2	68.0-76.0	13.0-15.0	0.6-1.0	(Tye *et al*. 2016)
Kenaf stalk fiber	0.5	44.0-63.0	18.0-21.0	15.0-19.0	(Tye *et al*. 2016)
Kenaf core	0.3	46.0-52.8	33.0-47.2	20.0-20.3	(Tye *et al*. 2016)
Leaf fiber					(Tye *et al*. 2016)
Abaca	0.1	61.0-70.1	21.0-22.0	5.7-12.0	(Tye *et al*. 2016)
Sisal	0.3	43.0-78.0	10.0-13.3	4.0-12.0	(Tye *et al*. 2016)
Pineapple	28	75.3	13.3	9.8	(Abraham *et al.* 2011)
Banana fiber	145	70	19.6	5.7	(Abraham *et al.* 2011)
Curaua fiber	< 0.1	73.6	9.9	7.5	(Spinacé *et al.* 2009)
Lotus leaf stalk	3 (China)	34.6	19.2	25.4	(Chen *et al.* 2015)
Roselle fiber	-	58-65	16-23	6-10	(Kian *et al.* 2017)
Seed hair fiber					
Cotton fiber	25	80.0-96.0	2.0-20.0	0.0-1.0	(Tye *et al*. 2016)
Kapok fiber	0.1	50.7-64.0	23.0-49.3	13.0-13.4	(Tye *et al*. 2016)
Areca nut fiber	-	34	21	32	(Chandra *et al.* 2016)
Coconut	62	39.3	2	49.2	(Abraham *et al.* 2013)
Wood and root					
Rubberwood	(3 mill ha)	42-48	18-22	27-31	(Jonoobi *et al.* 2011)
Indian screw tree	-	71	3.1	21	(Chirayil *et al.* 2014)
Achira fiber residue	-	19	16	3	(Andrade-Mahecha *et al.* 2015)
Fruit/legume					
Citrus	124	15	18 + 25 (pectin)	-	(Mariño *et al.* 2015)
Soybean	335	55-57 (hull)	12-23 (hull)	16-20 (hull)	(Alemdar & Sain 2008)
Soybean straw	-	35	17	22	(Martelli-Tosi *et al.* 2017)

It is somewhat difficult to estimate the reasonable volume information for certain feedstock materials in Table 3, so their values are not listed. The reader can get more specific volume information on the varying feedstocks (Bentsen *et al.* 2014; Kim and Dale 2004; Prasad *et al*. 2007; Sarkar *et al*. 2012; Väisänen *et al.* 2016); however, the authors mostly relied on the information provided by one reference (Tye *et al.* 2016). It is interesting to note that many agricultural residues, counting in many million tons, are not fully utilized, and most of these materials have been considered and handled as agro-waste. Another observation is that the bast fiber production is very small compared to agro-waste. Many bast fibers are produced from plants that only yield the fibers, while the other parts of the plants have no economic benefits. However, plants such as jute, hemp, and flax not only provide cellulose nanofibers, but their seeds and leaves can also be used for medical or food applications. Bast fibers are included in Table 3 because these materials are ideal feedstocks for nanocellulose production.

Historically, bast fibers are not considered to be waste and have been used for numerous products in many parts of the world. Agro-waste materials from fruits and legumes (*e.g.*, from coconuts, citrus fruits, pineapple, soybean, bananas) also stand out as largely underutilized resources, having the specific benefit of being collected at the manufacturing site with no additional labor cost.

Besides the information provided in Tables 2 and 3, one can consider the use of other natural fibers such as cassava, vegetable ivory, and tagua nut as viable feedstocks for nanocellulose production. Cassava (*Manihot esculenta*) is a main source of carbohydrate grown in sub(tropical) areas. Besides cassava bagasse, cassava peels also consist of cellulose (~38%), hemicellulose (24%), and lignin (~8%). It has been reported that alkaline treatment followed by bleaching could produce cellulose nanofibers from cassava peels (Widiarto *et al.* 2019). However, some literature reported lower cellulose (10%) and hemicellulose (29%) contents in cassava bagasse, which implies a lower yield of nanocellulose production if chosen as a feedstock (Edhirej *et al.* 2017). It is known that most agro-industries dealing with cassava typically produce tons of solid waste after separating the starch from the roots, and such waste is not considered to have high economic value. Another interesting case is the genus *Phytelephas*, which includes several kinds of palm trees, including the tagua-like *Phytelephas aequatorialis* that produces vegetable ivory seeds. Vegetable ivory seeds (from Manaus, Brazil) are composed of nearly 82% holocellulose (cellulose + hemicellulose) and over 14% lignin (da Silva *et al.* 2018). Carvajal-Barriga *et al.* (2022) used the sulfuric acid hydrolysis method followed by ultrasonication to produce nanocellulose from ivory seeds. They reported that stable nanocellulose gel (1% solid content) could be obtained after 4 h of hydrolysis at 60 °C using 8 M H_2SO_4 (Carvajal-Barriga *et al.* 2022). Another example, using green vegetable waste such as lettuce, leek, and artichokes as feedstocks, was demonstrated by Sanchez-Salvador *et al.* (2022b). They showed that by using several runs (up to six passes) of high shear through a high-pressure homogenizer, they could create lignocellulose micro- and nanofibrils (LCMNF) from these feedstocks.

NANOCELLULOSE PREPARATION PROCESSES FOR AGRO-WASTE AND NON-WOODY NATURAL PLANTS

In the subsections that follow, some details of the different nanocellulose production processes from various agro-waste and non-woody natural plants are summarized based on the following plant families: grasses, seed hair fibers, bast fibers, leaf fibers, certain wood, and roots (quite different from conventional woody plants), fruits and legumes. This review mainly focuses on land plants and will not discuss the production of nanocellulose from algae.

Grasses

Grasses feature tiny, inconspicuous blooms and narrow leaves with parallel veins. Typically circular, the stems contain noticeable joints or bulges where the leaves attach (nodes). Grasses are usually hollow, except at the nodes (Brown 1979). Selected examples of grasses are summarized as follows (an overview of nanocellulose production processes for grasses are given in Table 4).

Maize

Maize (*Zea mays*), also called corn or Indian corn, is a cereal plant of the grass family (Poaceae) with edible grain. One of the most frequently grown food crops in the world, it is a domesticated plant that was first grown in the Americas. After harvest, the major agro-waste of maize is corn stover, which consists of leaves, stalks, cobs of corn, and the nongrain part of harvested corn. Other weeds and grasses may also be present in the stover. Nanocellulose production procedures have been published using all parts of the maize plant. For example, using corn stover as a feedstock, one study applied a mild H_2SO_4 (0.5 wt%) solution pretreatment, followed by deacetylation with hot 0.4 wt% NaOH, and then steam explosion at 150 °C (Chen *et al.* 2013). With corn cobs as a feedstock, it was first treated with hot (80 °C) alkaline using 1 M NaOH for 2 h, followed by 0.6 wt% $NaClO_2$ for 2 h at 80 °C, and then high-pressure homogenization (Shogren *et al.* 2011). In another study, corn stalks were first delignified using a $NaClO_2$/acetic acid mixture at 70 °C for 6 h, followed by combined TEMPO oxidation and high pressure homogenization treatments (Boufi and Chaker 2016). Another procedure to produce nanocellulose from corn stalks involved the use of organosolv pulping approach with 40% ethanol at 165 °C for 1 h, followed by bleaching with acidic $NaClO_2$, and then TEMPO oxidation *(Balea et al*. 2017).

Oat

Oat (*Avena sativa*) also belongs to the grass family of Poaceae. Oats can be consumed by humans as oatmeal and oat milk, but they are also utilized as cattle feed. Its agro-waste includes oat hull fibers, which is also a suitable feedstock for nanocellulose production. For example, one study demonstrated that oat hull fibers could be first treated with 0.1 M NaOH for 1 h at 30 °C, followed by 0.1 N HNO_3 for 1 h at 85 °C, and subsequently by delignification procedure using 3 wt% H_2O_2 for 1 h at 70 °C, and then oxidized by TEMPO oxidation to obtain CNF materials (Valdebenito *et al.* 2017).

Rice

Another valuable food crop is rice, which also belongs to the grass family of Poaceae. The seeds of the grass species *Oryza glaberrima* (African rice) and *Oryza sativa* are the component of rice that can be eaten (Asian rice). The major agro-waste after harvest is rice straw, which has been shown to be an excellent feedstock for nanocellulose production. Jiang and Hsieh (2017) have published a comprehensive review, demonstrating the use of various methods to extract CNF from rice straw.

Table 4. An Overview of Some Nanocellulose (CNF) Production Processes for Grasses

Grass	Pretreatment Procedure	Pulping Procedure	Alkali Treatment	Bleaching	Hydrolysis	TEMPO Oxidation	Pulverizing Method	Reference
Corn stover	H_2SO_4 (0.5 wt%)	-	0.4 wt% NaOH (deacetylation)	-	-	-	Steam explosion	(Chen *et al.* 2013)
Corn cob	-	-	1 M NaOH	D			Homogenization	(Shogren *et al.* 2011)
Corn stalk	-	-	-	D	-	T	Homogenization	(Boufi & Chaker 2016)
Corn stalk	-	Organo-solv: 40% ethanol	-	D	-	T	Homogenization	(Balea *et al.* 2017)
Out hull	-	-	0.1 M NaOH f. by 0.1 M HNO_3	P	-	T	Homogenization	(Valdebenito *et al.* 2017)
Rice straw	Dewaxing (1)	-	5 wt% KOH (3, 2)	D (2, 3)	-	T (4)	Shear mixing (5)	(Abe & Yano 2009; Chaker *et al*. 2014; Hassan *et al*. 2012; Jiang & Hsieh 2017; Nasri-Nasrabadi *et al*. 2014)
Wheat straw	-	-	2 wt% NaOH + 10-12 wt% NaOH	P	1 M HCl	-	Steam explosion	(Kaushik & Singh 2011)
Wheat straw	Dewaxing	-	2 wt% KOH	D	-	-	Ultrasonification	(Chen *et al.* 2011b)
Wheat straw	-	-	17.5 wt% KOH	-	1 M HCl	-	Cryo-crushing	(Alemdar & Sain 2008)
Wheat straw	-	A	-	D	-	T	-	(Boufi & Chaker 2016)
Wheat straw	-	A	-	D	-	-	Enzymatic treatments + various pulverizing treatments	(Espinosa *et al.* 2020)
Bagasse fiber	-	Kraft pulping	-	-	-	-	Homogenization	(Hassan *et al*. 2012)

Bagasse fiber	-	Kraft pulping	-	-	-	-	Enzymatic treatment + grinding	(Liu *et al*. 2018)
Bagasse fiber	-	AQ	-	DPD	-	-	Grinding	(Heidarian *et al*. 2016)
Bagasse fiber	Steam explosion	-	Hydrothermal + 0.1 M NaOH	P	-	-	Ultrasonification	(Feng *et al*. 2018)
Bamboo fiber	Dewaxing (1)	-	2 wt% KOH (3)	D (2)	1 M HCl (4)	-	Ultrasonification	(Chen *et al*. 2011b)
Bamboo fiber	-	Kraft pulping	-	-	-	T	Microfluidization	(Zhang *et al*. 2012)
Bamboo fiber	-	NOP	-	-	-	-	Alkalization, ultrasonification	(Sharma *et al*. 2017b)
Spinifex fiber	-	-	2 M NaOH	D	-	-	Homogenization	(Amiralian *et al*. 2015)
Spinifex fiber	-	NOP	-	-	-	-	Alkalization, ultrasonification	(Sharma *et al*. 2018a)
Spinifex fiber	-	-	2 M NaOH	D	-	T	Ultrasonification	(Zhan *et al*. 2019)
Elephant grass	-	-	-	D + APS	-	T	-	(Yang *et al*. 2019)

D: sodium chlorite ($NaClO_2$) bleaching; P: peroxide (H_2O_2) bleaching; APS: ammoniumpersulfate ($(NH_4)_2S_2O_8$) bleaching; A: soda pulping; AQ: soda pulping with anthraquinone; NOP: nitro-oxidation process. Process operations from left to right and other process orders are indicated by digits in this table.

In this review, the authors argued that the most common method involved the steps of dewaxing, bleaching (with $NaClO_2$), followed by an alkaline pulping treatment using 5 wt% KOH (or in a reverse order), and finished with the combined TEMPO oxidation and shear mixing/grinding methods (Abe and Yano 2009; Chaker *et al.* 2014; Hassan *et al*. 2012; Nasri-Nasrabadi *et al.* 2014).

Rice straw refers to the stalks or stems of the rice plant that are left behind after the rice grains have been harvested. Rice straw can be used as a viable feedstock for nanocellulose production using different methods. Rice husk, on the other hand, is the outer hard cover that protects the rice grain, and it is also considered as an agro-waste. Rice husk contains about 35 to 40% cellulose.

Shahi *et al.* (2021) demonstrated that CNF can be obtained from rice husk using ultrasonic assisted method in combination with TEMPO oxidation. The resulting CNFs could be incorporated into polyimide substrates to create self-standing thin films as digital electrodes by drop casting. The resulted films can detect water-soluble gases including acetone, ammonia, methane, and hydrogen sulfide at room temperature.

Many biomass feedstocks contain some levels of silica particles. These silica particles can lead to issues in pulping. For example, rice husk and rice straw typically have a high level (sometimes 75%) of silica, which makes it difficult for composting or enzymatic hydrolysis. It is thus vital to choose an appropriate pretreatment method to remove silica before the oxidative treatment of cellulose. Khaleghian *et al.* (2017) tested different alkali treatments and found that the removal of silica from the rice straw was achieved efficiently by using highly concentrated sodium carbonate (> 91%). While the organosolv treatment could not remove silica, the lignin content in rice straw could be largely eliminated (Khaleghian *et al*. 2017). Ludueña *et al.* (2011) reported that rice husk typically contains silica at a level between 15 and 17%, and that it should be removed *via* chemical methods before being processed into cellulose nanofibers. To effectively remove silica from rice husk, Daifullah *et al.* (2004) demonstrated an easy procedure by using an alkaline (KOH) treatment followed by acidic (HCl) precipitation. Subsequently, by choosing an appropriate chemical treatment, nanocellulose can be produced. However, sequential treatments can often cause issues. Luduena *et al.* (2011) noticed that in the first stage of treatment (KOH + HCl), while silica could be removed, cellulose was partially converted into type II and hemicellulose was also eliminated. However, the components of lignin and wax could remain in the material. After the subsequent treatment with $NaClO_2$, the results indicated that the final nanocellulose possessed the cellulose II structure instead of conventional cellulose I (Ludueña *et al.* 2011).

Sorghum

A genus of flowering plants belonging to the Poaceae grass family is sorghum (*Sorghum bicolor*). The major agro-waste components of sorghum after harvest are sorghum leaves and stems. Although the literature search did not reveal any study using conventional processes to produce nanocellulose from sorghum waste, the study of Pennells *et al.* (2021) indicated that twin-screw extrusion, a continuous material processing method well-established within polymer, food and pharmaceutical processing, is an effective means to defibrillate sorghum residues.

Wheat

Wheat is a grass that is mostly grown for its seed – a cereal grain. Wheat is a worldwide staple food, also belonging to the Poaceae family. There are numerous varieties of wheat, which collectively make up the genus *Triticum*. The most widely grown wheat is *T. aestivum*. The stalk of wheat that is left over after the grains are harvested is known as wheat straw, and it is typically thrown away. Farmers in some countries often burn it, endangering the public's health and adding to air pollution. Different procedures to produce nanocellulose from wheat straw have been demonstrated. In one study, wheat straw was soaked with alkali solutions in two steps (first with 2 wt% NaOH overnight and then with 10-12 wt% NaOH), followed by bleaching with 8 wt% H_2O_2 overnight, hydrolysis with 1.0 M HCl at 60°C for 5 h, and a steam explosion approach (Kaushik and Singh 2011; Kaushik *et al.* 2010). In another study, wheat straw was first dewaxed and then treated with acidified $NaClO_2$ at 75 °C for 1 h until the fibers became white (Abe *et al.* 2007). The recovered fibers were then treated with 2 wt% KOH at 90 °C for 2 h to remove hemicellulose, after which ultrasonification was applied to produce nanocellulose (Chen *et al.* 2011a). In another study, wheat was treated with 17.5 wt% NaOH for 2 h, after which it was subjected to hydrolysis by 1 M HCl at 80 °C for 2 h. Finally, the treated fibers were subjected to cryo-crushing to induce defibrillation and produce nanocellulose (Alemdar and Sain 2008). In a different approach, chemical soda pulping with 5 wt% NaOH (2 h at 70°C) was used to treat wheat straw, followed by bleaching with acidified $NaClO_2$ at 70°C for 6 h (Boufi and Gandini 2015). Alternatively, soda pulping followed by the enzymatic treatment was also demonstrated to produce nanocellulose. Both approaches avoided the use of TEMPO oxidation (Espinosa *et al.* 2019).

Sugarcane

Sugarcane (*Saccharum* spp.) is another plant belonging to the Poaceae family, in the class of monocotyledons. Bagasse is the fibrous, dry pulp that remains after the juice from sugarcane stalks is extracted. Bagasse is often used as a biofuel for production of heat, energy, and electricity, as well as for manufacturing of pulp and building materials. The relatively simple methods to produce nanocellulose from bagasse fibers (Fontes *et al*. 2021) are to defibrillate commercially bleached kraft pulps with a high-power grinder (Hassan *et al.* 2012) or with an enzymatic treatment (De Campos *et al.* 2013; Liu *et al.* 2018). In one study, chemical pulping using soda/anthraquinone (AQ) and ECF bleaching approach followed by grinding was demonstrated to produce nanocellulose from bagasse fibers (Heidarian *et al.* 2016). In another approach, steam explosion treatments followed by an alkaline hydrothermal treatment, subsequent H_2O_2 bleaching and mechanical defibrillation was demonstrated (Feng *et al*. 2018).

Bamboo

Bamboo (*Dendrocalamus strictus*) is a group of woody perennial evergreen plants in the grass family of Poaceae. Some of its members are fast-growing giants, forming the largest members of the grass family. Bamboo fibers are an ideal source to produce nanocellulose. The typical procedures for nanocellulose production are as follows. In one approach, the dewaxed fibers were bleached with acidic sodium chlorite at 75 °C for 1 h, where the breaching treatments were repeated 5 times. After bleaching, the bamboo fibers were treated by 2 wt% KOH extraction at 90 °C for 2 h to remove hemicelluloses, and then with 1 wt% HCl at 80 °C for 2 h, before subjecting the treated fibers with ultra-sonification (Chen *et al*. 2011a,b). In a simpler approach, bleached kraft bamboo pulps were TEMPO oxidized followed the defibrillation treatment using a microfluidizer (Zhang *et al.* 2012). The production of nanocellulose from bamboo fibers was also demonstrated by the simple nitro-oxidation process using a mixture of HNO_3 and $NaNO_2$ in a single reactor (Sharma *et al.* 2017b).

Spinifex

Spinifex (triodia) is a large genus of perennial coastal plants in the grass family of Poaceae. Nanocellulose can be delignified with 2 M NaOH at 80 °C for 2 h and then bleached with acidic $NaClO_2$ at 70 °C. The mild alkaline treatment leaves a pulp with high hemicellulose content (42%), which makes the defibrillation easy without a separate oxidation stage (Amiralian *et al*. 2015). However, TEMPO oxidation has also been used in this preparation method (Zhan *et al.* 2019). Finally, the manufacture of nanocellulose from spinifex has been demonstrated by the simple nitro-oxidation process using HNO_3 together with $NaNO_2$ in different ratios, as reported by Sharma *et al.* (2018a).

Recently, it has been demonstrated that spinifex can provide "effortless extractability" to produce CNF. For example, after mild pulping with NaOH and just one run through a high-pressure homogenizer at relatively low pressure, it was discovered that *T. pungens* spinifex, an Australian grass, may easily be used to make high aspect ratio CNF with a very narrow cross-sectional dimension (2 to 10 nm) (Amiralian *et al*. 2015). In other words, with spinifex, one can largely eliminate the typical chemical and mechanical pretreatment steps required in contemporary protocols. Furthermore, one can tune the aspect ratio through mechanical energy (*e.g*., by altering the number of passes in high pressure homogenizer). It has been hypothesized that an unusually high remnant hemicellulose content (approximately 42% in spinifex) appears to be the key factor in this more amenable fibrillation trait, effectively toughening the nanofibers and rendering them more fracture-resistant during the conditions of high shear, turbulence, and cavitation imposed during homogenization.

Other grasses

Bermuda grass (*Cynodon dactylon*), also in the family of Poaceae, is native to most of the eastern hemisphere. This grass is an herbaceous perennial crop that is widely known in the U.S. There are, to our knowledge, no publications on nanocellulose manufacture using coastal Bermuda grass as a feedstock.

Elephant grass (*Miscanthus* × *giganteus*), also known as the giant miscanthus, is a sterile hybrid of *Miscanthus sinensis* and *Miscanthus sacchariflorus* (family of Poaceae). It is a perennial grass that may reach heights of more than 4 meters in a single growing season and has stems that resemble bamboo. Delignification procedures have been successfully applied to elephant grass stalks. For example, bleaching was carried out by using $NaClO_2$/acetic acid at 70 °C for 2 h, followed by the treatment of 1 M ammonium persulfate at 90 °C for 16 h as the second stage. To obtain nanocellulose, a TEMPO oxidation procedure was used to delaminate the bleached fiber (Yang *et al.* 2019).

Switchgrass (*Panicum virgatum*) is a perennial warm season bunchgrass native to North America, occurring naturally from 55 north latitude in Canada southward into the United States and Mexico (family of Poaceae). To the best of our knowledge, there are no publications on the manufacture of nanocellulose from switchgrass.

Bast Fibers

Typical bast fibers are fine and flexible. They are often referred to as "soft" fibers to differentiate them from leaf fibers, which are "hard", meaning more robust and less flexible. Bast fibers are multicellular, composed of bundles of single cells, wherein the individual fibers are held together by lignin, pectin, and a small amount of protein.

Generally, bast fibers tend to be longer than other fibers within the plant. They exist in the inner bark of the plant (Dalle Vacche *et al*. 2021). The manufacturing procedures for nanocellulose production from bast fibers are shown in Table 5.

Flax

Flax (*Linum usitatissimum*) is a plant of the Linaceae family, which can grow to about 1 m tall. In one study, flax fibers were first treated by retting, and subsequently soaked with 17.5% NaOH for 2 h, followed by hydrolysis in 1 M HCl at 60 to 80 °C, and then treated with 2% NaOH for 2 h at 60 to 80°C to produce nanocellulose (Bhatnagar and Sain 2005). Chen *et al.* (2011a) investigated the nanocellulose production from four different plants (including flax fibers) using a classical delignification procedure, *i.e.*, acidic $NaClO_2$ treatment followed by strong KOH extraction. With this method, it was noted that wood pulp, wheat straw and bamboo fibers all yielded nanocellulose with a cross-sectional dimension between 10 and 40 nm under the same conditions, whereas flax fibers could not be uniformly nanofibrillated. The failure to produce nanocellulose from flax fibers using this procedure was attributed to their high cellulose content (Chen *et al.* 2011a). In another study, nanocellulose was successfully produced from flax fibers using soda-pulping with 16% NaOH at 165°C, followed by bleaching with 1.5% $NaClO_2$. The material was then treated by TEMPO oxidation (degree of oxidation was 0.5 mmol/g) and completed with a high pressure homogenization treatment (Alila *et al.* 2013).

Hemp

Hemp, a type of the cannabis sativa plant (in the family of Cannabaceae), is grown primarily for industrial applications. Hemp is one of the fastest growing plants, and it was one of the first plants to be spun into useful fibers thousands of years ago. Several studies have been reported on the procedures to produce nanocellulose. For example, in one study, hemp fibers were first soaked in 17.5% NaOH for 2 h at room temperature, followed by an acid hydrolysis in 1 M HCl at 60 to 90°C, and then treated with 2% NaOH for 2 h at 60-90 °C before fiber defibrillation. (Bhatnagar and Sain 2005). A similar method was also reported by a different group (Wang *et al.* 2007). In a study by Alila *et al*. (2013), the pulping method was first used to treat raw hemp with 16% NaOH at 165°C. The resulting hemp pulp was then bleached with 1.5% $NaClO_2$, followed by the TEMPO oxidation treatment to yield carboxyl fibers with a degree of oxidation around 0.5 mmol/g. Nanofibers were subsequently obtained by homogenization (Alila *et al.* 2013).

Jute

Jute belongs to the family of Malvaceae, and it can be obtained from the plants *Corchorus olitorius* and *Corchorus capsularis*. Typically, jute grows in hot and humid climates of the equatorial, tropical, and sub-tropical zones. Studies have demonstrated that nanocellulose can be easily produced from jute. For example, Alila *et al*. (2013) demonstrated that nanocellulose could also be produced using the same approach for treating hemp fibers.

Abraham *et al.* (2011) reported the use of steam explosion, followed by $NaClO_2$ bleaching and acid treatment (5% oxalic acid) to yield nanocellulose. In contrast, Baheti *et al*. (2012) used a cold alkali soaking pretreatment (in 18% NaOH at room temperature for 2 h) followed by hot acid (H_2SO_4, 1 M at 80°C) and then alkaline treatments (4% NaOH at 80°C), where the treated fibers were defibrillated by ball milling to produce nanocellulose.

Table 5. Manufacturing Procedures for CNF Materials from Bast Fibers

Bast Fibers	Pretreatment Procedure	Pulping Procedure	Alkali Treatment	Bleaching	Hydrolysis	TEMPO Oxidation	Pulverizing Method	Reference
Flax fiber	Retting (1)	-	17.5% NaOH (2) 2% NaOH (4)	-	1 M HCl (3)	-	Cryo-crushing	(Bhatnagar & Sain 2005)
Flax fiber	Dewaxing	-	2% KOH (2) 5%KOH (4)	D (1) D (3)	-	-	Ultrasonication	(Chen *et al.* 2011a)
Flax fiber	-	A	-	D	-	T	Homogenization	(Alila *et al.* 2013)
Hemp fiber	-	-	17.5 NaOH (1) 2% NaOH (3)	-	1 M HCL (2)	-	Cryo-crushing	(Bhatnagar & Sain 2005) (Wang *et al.* 2007)
Hemp fiber	-	A	-	D	-	T	Homogenization	(Alila *et al.* 2013)
Jute fiber	-	A	-	D	-	T	Homogenization	(Alila *et al.* 2013)
Jute fiber	Steam explosion	-	-	D	5% Oxalic acid	-	Mechanical defibrillation, ultrasonification	(Abraham *et al.* 2011)
Jute fiber	-	-	18% NaOH (1) 4% NaOH (3)	-	1 M H_2SO_4 (2)	-	Ball milling	(Baheti *et al.* 2012)
Jute fiber	-	O-solv: formic acid/acetic acid/HCl	-	-	Acetylation: acetic acid/nitric acid	-	Homogenization	(Serrano *et al.* 2011)
Jute fiber	-	NOX	-	-	-	-	Alkali treatment + ultrasonification	(Sharma *et al.* 2017b)
Ramie fiber	-	Alkaline O-solv: ethanol-water (1)	2% NaOH (3)	D (2)	-	-	Masuko colloider	(Marinho *et al.* 2020)
Kenaf stalk fiber	Retting	AQ	-	DEPD	-	-	Cryo-crushing	(Jonoobi *et al.* 2009)
Kenaf stalk fiber	Retting	AQ	-	DEPD	-	-	Masuko colloider	(Karimi *et al.* 2014)
Kenaf core	Retting	AQ	-	DEPD	-	-	Homogenization	(Joonobi *et al.* 2010)
Kenaf bast fiber	Retting	AQ	-	DEPD	-	-	Masuko colloider	(Babaee *et al.* 2015)

D: sodium chlorite, NaClO; P: peroxide, H_2O_2; E: alkali stage; A: soda pulping; AQ: soda pulping with anthraquinone. Process operations from left to right and other process orders are indicated by digits in the table.

In another study, the process of organosolv pulping with formic acid/acetic acid/HCl mixtures followed by acetylation and homogenization was demonstrated to produce jute nanofibers (Serrano *et al.* 2011).

Recently, the authors' lab demonstrated that nanocellulose can be produced from raw jute using the simple nitro-oxidation process with HNO_3 and $NaNO_2$ mixtures at a moderate temperature (*e.g.*, 50 °C), where the process combined the steps of pulping and cellulose oxidation (Sharma *et al.* 2017b).

Ramie

Eastern Asia is home to the nettle family Urticaceae flowering plant known as ramie (*Boehmeria nivea*). It is a perennial herbaceous plant with a height range of 1.2 to 2.5 meters. Ramie is another one of the oldest fiber crops, having been used for at least 5,000 years, mainly for fabric production. There are very few studies on nanocellulose production from ramie. However, a recent study demonstrated the use of alkaline (6% NaOH) organosolv pulping (ethanol/water mix) at 160 °C for an hour, followed by two bleaching steps (*i.e.*, a $NaClO_2$ treatment and an alkaline treatment using 2% NaOH) to yield nanocellulose from ramie (Marinho *et al*. 2020).

Kenaf

Kenaf (*Hibiscus cannabinus*), from the family of Malvaceae, is also called Deccan hemp and Java jute. Kenaf is in the genus Hibiscus, native to Southern Asia, India, Bangladesh, Thailand, and parts of Africa, though its exact origin is unknown. The name kenaf applies not only to the plant, but also to the fiber obtained from the plant. Kenaf is one of the allied fibers of jute, showing similar characteristics. There are several studies demonstrating the approach of nanocellulose production from kenaf stalk fibers. For example, Jonoobi *et al*. (2009) used 25% NaOH/AQ at 160 °C for 2 h to prepare fiber pulp, and then a 3-stage treatment involving (1) 2% $NaClO_2$ and 2% CH_3COOH solution, (2) 1.5% NaOH and 1% H_2O_2 solution, and (3) 1.25% $NaClO_2$ and 3% CH_3COOH solution to complete the bleaching treatment. Karimi *et al.* (2014) used the Masuko super-colloider to prepare nanocellulose from both unbleached and bleached kenaf, whereas Jonoobi *et al.* (2009) used cryo-crushing and high-pressure homogenization methods for nanofibers production. Additionally, Jonoobi et al. (2009, 2010) and Babaee *et al.* (2015) also demonstrated the approach using NaOH/AQ pulping, subsequent bleaching, followed by mechanical defibrillation treatments to produce nanofibers from kenaf core.

Leaf Fibers

Although leaf fibers and bast fibers are both naturally derived fibers from plants, they come from different parts of the plant and have distinct characteristics. For example, leaf fibers are derived from the leaves of the plant, located in the vascular bundles of the leaves. In contrast, bast fibers are located in the inner bark (phloem) of the plant. Leaf fiber is mostly used for cordage (*i.e.*, rope production), and is the toughest plant fiber, which is most likely due to its high lignin content when compared to other plant fibers. Among leaf fibers, sisal and abaca are the primary fibers that are harvested and sold. An overview of the manufacturing procedures of nanocellulose from leaf fibers is summarized in Table 6.

Table 6. An Overview of Manufacturing Procedures for Nanocellulose Production from Leaf Fibers

Leaf Fiber	Pretreatment Procedure	Pulping Procedure	Alkali Treatment	Bleaching	Hydrolysis	TEMPO Oxidation	Pulverizing Method	Reference
Abaca fiber	-	A	-	D	-	T	Homogenization	(Alila *et al.* 2013)
Sisal fiber	-	A	-	D	-	T	Homogenization	(Alila *et al.* 2013)
Sisal fiber	-	A	-	D	-	-	Microfluidization	(Siqueira *et al.* 2009)
Pineapple leaf fiber	-	-	2% NaOH	D	-	-	Ball milling	(Ravindran *et al.* 2019)
Pineapple leaf fiber	Steam explosion in 2% NaOH	-	-	6xD	Oxalic acid, steam explosion	-	Mechanical defibrillation	(Abraham *et al.* 2011; Cherian *et al.* 2011; Cherian *et al.* 2010; Deepa *et al.* 2015);
Banana rachis	Bio-fermentation	Organosolv 70% acetic ac.	12 M NaOH + 1.5% H_2O_2	(D)	-	-	Homogenization	(Zuluaga *et al.* 2007; Zuluaga *et al.* 2009)
Banana rachis	-	-	2% NaOH + steam ex.	D	5% Oxalic acid + steam explosion	-	Mechanical defibrillation	(Abraham *et al.* 2011; Deepa *et al.* 2011; Deepa *et al.* 2015)
Banana fiber	-	NOX (2)	12% NaOH (1)	-	-	-	-	(Kumar *et al.* 2019)
Banana pseudo stem	-	Liquefaction with PEG/Glycerol	-	D	-	T	-	(Meng *et al.* 2019)
Banana peel	-	-	5% KOH	D	-	-	Homogenization	(Pelissari *et al.* 2017; Pelissari *et al.* 2014)
Curaura fiber	-	-	-	D	-	-	Enzymatic treatment + ultrasonification	(De Campos *et al.* 2013)
Curaura fiber	-	-	-	D + 5% NaOH	-	-	Mechanical defibrillation	(Motta Neves *et al.* 2020)
Lotus leaf fiber	-	-	5% KOH (2)	D (1)	1 M HCl (3)	-	Ultrasonification	(Chen *et al.* 2015)

D: sodium chlorite, NaClO; A: soda pulping; NOX: nitro-oxidation. Process operations from left to right and other process orders are indicated by digits in the table.

Abaca

Abaca binomial (*Musa textilis*) is a species of banana native to the Philippines and typically grown as a commercial crop in the Philippines, Ecuador, and Costa Rica. Abaca is in the banana family Musaceae. The plant, also known as Manila hemp, has great economic importance because fiber can be extracted from the leaf-stems. Nanocellulose can also be readily produced from this crop's fibers. A typical production approach has been demonstrated using a pulping treatment with 16% NaOH at 165 °C, followed by bleaching with 1.5% $NaClO_2$, then a TEMPO-mediation oxidation step, and completed with a high pressure homogenization process (Alila *et al.* 2013).

Sisal

Sisal (*Agave sisalana*) is an agave species of the Asparagaceae family. The major sisal crop growing countries are Mexico, Brazil, Tanzania, and Kenya. Several studies have been reported to produce nanocellulose from sisal fibers. In addition to the approach discussed in (Alila *et al.* 2013), another study showed that a milder procedure using 4% NaOH at 80 °C for 2 h is also effective to delignify sisal fibers. After the fiber pulp was bleached with acidic $NaClO_2$ for 4 times, the bleached pulp can be defibrillated by a high pressure homogenization process. (Siqueira *et al.* 2009)

Pineapple

Pineapple (*Ananas comosus*) is an herbaceous perennial plant. It is fruit bearing and belongs to the family of Bromeliaceae. Pineapple is native to tropical and subtropical America, but it was introduced in other tropical regions. The pineapple plant resembles the agave family, and similarly, nanocellulose can also be produced from pineapple leaf fibers. In one study, pineapple leaf fibers were first given an alkaline treatment (2% NaOH for 4 h at 100 °C), followed by an acidic $NaClO_2$ treatment, and then followed by ball milling to produce nanocellulose (Ravindran *et al*. 2019). In another study, the fibers were treated with steam explosion in 2% NaOH for 1 h. at high temperature. The fibers were then bleached with acidic $NaClO_2$ six times, after which the fibers were again steam exploded in oxalic acid and the resulting fibers were further mechanically dispersed (Cherian *et al*. 2010, 2011). Similar procedures as described in two earlier references have also been adopted to produce nanocellulose from pineapple fibers (Abraham *et al.* 2011; Deepa *et al.* 2015).

Banana

Bananas belong to the family of Musaceae, where the plants (order Zingiberales) consist of 2 major genera, such as Musa and Ensete, and with about 50 species native to Africa, Asia, and Australia. Banana is one of the most consumed fruits in the world, where its plants also produce large amounts of pseudostem and rachis residues that are rich in cellulose. Typical banana fibers can be obtained from the pseudostem of the banana plant, where the stem looks like a trunk. The pseudo stem is formed by the tightly packed overlapping leaf sheaths. Even though the pseudo stem is very fleshy and consists mostly of water, it is quite sturdy (a bunch can support 50 kg of weight or more).

Banana rachis is an excellent source to produce nanocellulose. In one study, the rachis was first subjected to biological fermentation, treated with 12 M NaOH/1.5% H_2O_2 at 45 °C for 14 h, and then subjected to a pulping treatment with 70% CH_3COOH at 120 °C for 15 min. The pulp suspension was defibrillated by homogenization to produce nanocellulose (Zuluaga *et al.* 2007). Some modifications of this procedure, including the adoption of $NaClO_2$ bleaching, were also investigated by this research group. In another study, banana fibers were first soaked in 2 M NaOH at 30 °C for 6 h and then subjected to steam explosion at 200 to 250 °C, followed by bleaching with acidic $NaClO_2$ at 50 °C for 1 h. The fiber pulp was then treated with 5% oxalic acid in a second steam explosion process (Abraham *et al.* 2011; Deepa *et al.* 2011) or a mechanical stirring process to yield nanocellulose (Deepa *et al.* 2015). In a different approach, banana fibers were directly treated with strong alkali (12% NaOH) followed by nitro-oxidation process (with HNO_3/$NaNO_2$) to produce nanocellulose (Kumar *et al*. 2019)

Nanocellulose has also been produced from banana pseudostem. In one study, a liquefaction step with poly(ethylene glycol) and glycerol was first used to treat banana pseudostem, where the treated fibers were subsequently bleached by acidic $NaClO_2$ at 75 °C for 1 h, followed by the TEMPO-mediated oxidation (Meng *et al.* 2019). Additionally, nanocellulose produced from banana peel has been investigated. Banana peel was soaked with 5% KOH for 14 h, followed by bleaching treatment of CH_3COOH/$NaClO_2$ at pH 5 at 70 °C for 1 h, and then defibrillated using high-pressure homogenization (Pelissari *et al.* 2014, 2017).

Curia

Curaua is a giant bromeliad, native to Amazonia and belonging to the pineapple plant family Bromeliaceae. Curaua is a rosette-forming herbaceous plant (as is the pineapple), from which fibers can be extracted. It has been used for various applications such as paper production, ropes, hammocks, and nets. Today, it is mainly used for the automotive industry. Nanocellulose can be readily produced from Curaua fibers. In one study, fibers were bleached with acidic $NaClO_2$ by suspending them in a solution containing 0.7% CH_3COOH and 3.3% $NaClO_2$ under stirring at 75 °C for 4 h. The bleached fibers were then subjected to enzymatic hydrolysis followed by sonification to produce nanocellulose. In another study, fibers were treated in a 12% NaClO solution with a 5% NaOH solution at 50 °C for 2 h, followed by mechanical defibrillation to create nanocellulose (Spinacé *et al*. 2009; Motta Neves *et al.* 2020).

Lotus

Nelumbo nucifera is a water plant, more commonly called Indian lotus, or water lily. It is also referred to as the sacred lotus, bean of India, or Egyptian bean. It is extremely widespread, with a native range that stretches from central and northern India (at elevations up to 1,400 m in the southern Himalaya), through northern Indochina, eastern Asia, and Russia. Nanocellulose can be readily produced from lotus leaf fibers. For example, in one study, lotus leaf fibers could be first bleached with 2% $NaClO_2$ at pH 4 at 75 °C, after which holocellulose was produced with 5% KOH at 90 °C for 2 h. This treatment was followed by another treatment of 1% HCl at 80 °C for 2 h to produce a highly purified lotus leaf fibers' cellulose fiber, which could be defibrillated into nanofibers by ultrasonification. (Chen *et al.* 2015).

Seed Fruits

In botany, fruits are the seed-bearing organs that develop from the ovary after flowering in flowering plants, sometimes referred to as angiosperms. The pathway that angiosperms disperse seeds is through their fruits. An overview of manufacturing procedures to produce nanocellulose from seed fruits are shown in Table 7.

Oil palm

Oil palm (*Elaeis guineensis*) is a species of palm, also called African palm, which belongs to the family of Arecaceae. It is native to West and Southwest Africa, specifically the area between Angola and Gambia. Oil palm is the principal source of palm oil. The global production of palm oil was about 75 million tons in 2020, with each ton of palm oil leaves producing 1.1 ton of oil palm empty fruit bunch (OPEFB). An oil palm tree may yield 8 to 12 fruit bunches every year. Each fruit bunch weighs between 10 and 25 kg, and once the oil is extracted, the remaining seed (OPEFB) causes a waste issue for the environment. Nanocellulose can be produced by several different approaches from this source. In one study, OPEFBs were first pulped with 12% NaOH/AQ, followed by acidic $NaClO_2$ bleaching at 70 °C for 3 h. The pulp was further treated by alkaline H_2O_2 and then another acidic $NaClO_2$ stage, where defibrillation of the fibers was accomplished by mechanical grinding (Wiley mill) or high-pressure homogenization (Jonoobi *et al*. 2011). In a more elaborate approach by Ferrer *et al*. (2012), three different pulping procedures were investigated: (a) soda-anthraquinone (NaOH-AQ) pulping at 170 °C for 30 min; (b) formic acid and HCl (Formosolv: 92.5% formic acid and 0.075 M HCl) for at 100 °C 60 min; and (c) formic acid and peroxide (Milox: 53% formic acid and 3% H_2O_2) at 80 °C for 165 min. The resulting pulp (in a never dried state) could be ion-exchanged to their Na-form, to promote the defibrillation, which was carried out by the combined treatment of mechanical beating and microfluidization (Ferrer *et al*. 2012). In another study, OPEFBs were treated by a more conventional approach, involving dewaxing, bleaching with $NaClO_2$ (70°C for 1 h), and alkaline extraction with 6% KOH 24 h at room temperature, followed by ultrasonification (Fahma *et al.* 2010).

Cotton

The cotton plant produces a boll, or protective casing, which is made of soft, fluffy staple fibers known as cotton. The cotton plant (*Gossypium* genus) belongs to the Malvacea family (also known as Mallow family). Cotton fiber doesn't need to be pulped because it is virtually entirely composed of cellulose. Native to tropical and subtropical regions of the world, including the Americas, Africa, Egypt, and India, the plant is a shrub. There are many publications on the production of nanocelluloses from cotton, mostly in the form of CNC, but few in the form of CNF. The cotton waste after processing is an excellent feedstock source to yield nanocellulose. In one study, chopped waste cotton was subjected to direct bleaching using a mixture of $NaOH/CH_3COOH$ and $NaClO_2$ (ratio 1:3), where the bleached fiber suspension was treated by steam explosion. After washing, the recovered fibers were treated by mild hydrolysis with oxalic acid and then subjected to high-pressure homogenization (Sangeetha *et al*. 2020).

Kapok

The kapok tree (*Ceiba pentandra*) is a towering rain forest tree, also called the Ceiba tree or silk cotton tree, also belonging to the family of Malvaceae. Kapok is the seed pod fluff of the tree. Kapok fibers from the pod are a good source to produce nanocellulose. In one study, kapok fibers were subjected to steam explosion in 2% NaOH at 110 to 120 °C. After this process, the fibers were subjected to delignification treatment using 1% $NaClO_2$ at 70 °C for 1 h, where the treatment was repeated several times. After washing and drying of the treated fibers, they were subjected to acid hydrolysis using 5% oxalic acid and then mechanical stirring to produce nanocellulose (Deepa *et al.* 2015)

Table 7. Manufacturing Procedures to Produce Nanocellulose from Seed Fruits

Seed Fruit	Pretreatment Procedure	Pulping Procedure	Alkali Treatment	Bleaching	Hydrolysis	Pulverizing Method	Reference
Oil palm empty fruit bunches (EFP)	-	AQ	-	DPD		Mechanical defibrillation	(Jonoobi *et al.* 2011)
Oil palm EFB	-	AQ	-	Formosolv + Milox treatment		Alkali mech. defibrillation + Microfluid.	(Ferrer *et al.* 2012)
Oil palm EFB	Dewaxed (1)	-	6% KOH (3)	D (2)		Ultrasonication	(Fahma *et al.* 2010)
Cotton fiber	-	-		D + Steam explosion	Oxalic acid	Homogenization	(Sangeetha *et al.* 2020)
Kapok fiber	-	-	Steam explosion in 2% NaOH	D	5% Oxalic acid	Mechanical defibrillation	(Deepa *et al.* 2015)
Areca nut husk fiber	Dewaxed	-	5% NaOH (1) 5% NaOH (4)		3.5 M HCl (2) 5 M HCl (5)	Grinding (3), Homogenization (6)	(Chandra *et al.* 2016)
Coconut husk fiber (coir)	-	-	Steam explosion in 2% NaOH	D	5% Oxalic acid	2nd Steam explosion. + sonification	(Abraham *et al.* 2013)
Coconut husk fiber (coir)	-	-	Steam explosion in 2% NaOH	D	5% Oxalic acid	Masuko grinder	(Deepa *et al.* 2015)

D: sodium chlorite, NaClO; AQ: soda pulping with anthraquinone. Process operations from left to right and other process orders are indicated by digits in the table.

Table 8. Manufacturing Procedures for Nanocellulose Production from Agricultural Residues in the Form of Wood and Roots

Plant	Pretreatment	Pulping Procedure	Alkali Treatment	Bleaching	Hydrolysis	Pulverizing Method	Reference
Oil palm tree			5% (2) KOH	D (1)		Masuko grinder	(Okahisa *et al.* 2018)
Rubber-wood tree		AQ		DPD		Grinding Homogenization	(Jonoobi *et al.* 2011)
Helicteres isora plant	Retting	A		D	10% Oxalic acid	Homogenization	(Chirayil *et al.* 2014)
Achira fiber			5% KOH (1) 5% KOH (3)	P (2)	1% HCl	Homogenization	(Andrade-Mahecha *et al.* 2015)

D: sodium chlorite, NaClO; P: peroxide, H_2O_2; A: soda pulping; AQ: soda pulping with anthraquinone. Process operations from left to right and other process orders are indicated by numbers in the table.

Areca

The areca palm (*Areca catechu*), which is found in much of the tropical Pacific Melanesia and Micronesia (Southeast and South Asia) and in some areas of east Africa, produces the areca nut as its seed. It is commonly referred to as betel nut, which belongs to the family of Arecaceae. Areca husk left behind after harvest can cause a foul odor and other biomass decay-induced problems. It has been demonstrated that areca nut husk fibers are a good feedstock to produce nanocellulose. In one study, the dried areca nut husk fibers were first dewaxed, subsequently treated with 5% NaOH at 50°C for 4 h, and then 3.5 M HCl at 50 °C overnight.

After mechanical grinding, the fibers were further treated with 5% NaOH at 50 °C for 4 h, and then 5 M HCl overnight. The resulting fibers were then bleached with acidic $NaClO_2$, followed by homogenization (with an Ultra Turrax homogenizer) to yield nanocellulose (Chandra *et al.* 2016).

Coconut

Coconut is the fruit of coconut palm (*Cocos nucifera*), a tropically grown palm tree in the Arecaceae family. The palm flowers monthly, and its fruits take one year to ripen. A mature palm tree can produce 50 to 100 coconuts each year. Coconut husk fibers (coir) is an excellent woody feedstock to produce nanocellulose. In one example study, coir fibers were first soaked in 2% NaOH at 25°C for 6 h, followed by steam explosion at 100 to 150°C. Coir fibers were then delignified by bleaching with acidic $NaClO_2$ at 50°C for 1 h, followed by a mild acid treatment using 5% oxalic acid, and then a second steam explosion step to produce nanocellulose (Abraham *et al*. 2013) A similar procedure was demonstrated by Deepa *et al*. (2015), where the coir fibers were first subjected to steam explosion in 2% NaOH (110 to 120°C) and then pulping by 1% $NaClO_2$ at 70°C for 1 h (several times). The pulp was subsequently subjected to acid hydrolysis with 5% oxalic acid and then by mechanical defibrillation using a Masuko grinder (Deepa *et al.* 2015).

Wood and Roots from Agricultural Residues

An overview of some manufacturing procedures for nanocellulose production from agricultural residues in the form of wood and roots is illustrated in Table 8.

Oil palm tree

The oil palm tree (*Elaeis guineensis*) itself is also a good source for nanocellulose production. One research group investigated different parts of the palm tree waste, including the mesocarp, the palm kernel without empty palm fruit bunch fibers, and the trunk as different feedstocks. These materials were all cyclically bleached using acidified $NaClO_2$ at 70 °C for 1 h until the fibers became white. After bleaching, the hemicellulose components were extracted using 5% KOH for at 80 °C for 2 h, and then delaminated using a Masuko-grinder. The authors observed that nanocellulose could be produced from all parts of the palm tree, though the resulting nanocelluloses exhibited variations in mechanical properties due to the different compositions and cellulose crystallinity of the different palm parts (Okahisa *et al.* 2018).

Rubberwood tree

Light-colored medium-density tropical hardwood can be extracted from a rubberwood tree, which is also called Pará rubber tree (*Hevea brasiliesis*), belonging to the family of Euphorbiaceae. These trees are cultivated in rubber plantations. Rubber trees have a 32-year economic life span in plantations, which is broken down into a 7-year immature stage and a 25-year productive stage before the trees are taken down. In the past, the cut trees were burned, but today they are increasingly used for furniture. As a result, rubberwood trees are commonly viewed as an "environmentally friendly" wood. Cut wood from rubberwood tree is a good feedstock for nanocellulose production. In one study, the rubberwood was first pulped with 12% NaOH/AQ followed by acidic $NaClO_2$ bleaching at 70 °C for 3 h (Jonoobi *et al.* 2011). The system was then treated with alkaline H_2O_2 and then another run of acidic $NaClO_2$. Fiber defibrillation was achieved through mechanical grinding (Wiley mill) or high-pressure homogenization.

Helicteres isora

Helicteres isora, a member of the Sterculiacea family, is sometimes referred to as the Indian screw tree. It is mainly found in Southern Asia and Northern Oceania, and it can be either a little tree or a huge shrub. The *Helicteres isora* plant is a reliable source to obtain nanocellulose. For example, one study has demonstrated the following route using barks of the plant as a feedstock. The tree barks were first subjected to biological retting, where the material was then treated in an autoclave in 2 M NaOH at 110 °C for 1 h. The resulting fibers were bleached using acidic $NaClO_2$ (repeated 6 times), followed by acid hydrolysis using 10% oxalic acid for 15 min (for 8 times), and then finally by high-pressure homogenization to produce nanofibers (Chirayil *et al.* 2014)

Achira

Achira (*Canna indica* L.) is a perennial plant, native of the Andes in South America. Since it is one of the 25 sources of starch consumed in the tropics, its cultivation has spread to many Asian nations. Achira fibers can be used to produce nanocellulose. In one study, achira fibrous residues were first treated with 5% KOH at room temperature for 14 h, after which the fibers were bleached with either 4% H_2O_2 (90°C) or with 0.25% peracetic acid (75°C), and then an alkaline treatment with 5% KOH (the process was repeated several times). Finally, the treated fibers were subjected to acid hydrolysis with 1% HCl at 80 °C for 1 to 2 h and were delaminated using high-pressure homogenization to yield nanocellulose (Andrade-Mahecha *et al.* 2015).

Fruits and Legumes

An overview of some manufacturing procedures to produce nanocellulose from fruits and legumes is summarized in this section (Table 9).

Citrus

A genus of flowering trees and shrubs in the Rutaceae family is called citrus. Citrus fruits including oranges, lemons, grapefruits, pomelos, and limes are produced by plants of this genus. Citrus waste can be a good feedstock for nanocellulose production, since citrus is composed of approximately 15% cellulose, 18% hemicellulose and 25% pectin; the remaining components include soluble sugars (15 to 20% sugars), proteins (6.5 to 8%), starch (4%), ash (4%), and a small fraction of fat, lignin and flavonoids (Mariño *et al.* 2015). Since the processing of citrus fruits is of large scale, the improper waste disposal can lead to a considerable environmental problem.

Orange peel is a good feedstock for nanocellulose production. Hideno *et al.* (2014) used the mechanical homogenization treatment to process orange peels, and then they treated the slurry with 2% NaOH at 80°C for 3 h. Subsequently, the filtered fibers were treated with a pectinase enzyme to remove the pectin component.

Table 9. Manufacturing Procedures for Nanocellulose Production from Fruits and Legumes

Fruit and Legume	Pretreatment Procedure	Pulping	Alkali Treatment	Bleaching	Hydrolysis	Pulverizing Method	Reference
Orange peel	Homo-genization		2 M NaOH and enzyme treatment			Masuko grinder	(Hideno *et al*. 2014)
Orange peel		A		D		Enzyme treat. + ultrasonification	(Mariño *et al*. 2015)
Orange peel	Dewax. (1)		6% NaOH (3)	P (2)		Ultrasonification	(Naz *et al.* 2016)
Soybean hull			17.5% NaOH (1) 2% NaOH (3)		1 M HCl (2)	Cryo-crushing (4)	(Alemdar & Sain 2008; Ferrer *et al*. 2016)
Soybean hull			Extrusion with 10% NaOH (1)	Peracetic acid (3)	2 steps with 2% H_2SO_4 (2) 2% H_2SO_4 (4)	Ultrasonification	(Debiagi *et al*. 2020)
Soybean straw			17.5% NaOH	P	2% H_2SO_4	Enzyme treat. + Ultraturrax+ ultrasonification	(Martelli-Tosi *et al*. 2018)

D: sodium chlorite, NaClO; P: peroxide, H_2O_2; A: soda pulping. Process operations from left to right and other process orders are indicated by digits in the table.

This was followed by autoclavation at 120 °C to deactivate the enzyme, followed by the removal of dissolved carbohydrates. The resulting fibers were then delaminated using a Masuko grinder (Hideno *et al.* 2014). In a different approach, the treatment of orange peels using soda cooking (4% NaOH at 120 °C for 20 min) was followed by 2% $NaClO_2$ bleaching (120 °C for 20 min), enzymatic treatment, and then ultrasonification to yield nanocellulose (Mariño *et al.* 2015). In an alternative approach, the citrus waste was treated with a H_2O_2 treatment at 80 °C in repeated sequences until a clear white product was obtained. Next the fibers were treated with 6% NaOH overnight, followed by ultrasonification (Naz *et al*. 2016). The resulting nanocelluloses differed, depending on the type of waste used and the processing conditions.

Soybean

Glycine max, also known as soybean or soya bean, is a type of legume that is indigenous to East Asia and is a member of the Fabaceae family. It is widely grown for its edible bean component, which has numerous usages. In the typical oil extraction process, soybeans are first screened to remove broken and damaged beans, as well as foreign materials, where soybean hulls are a byproduct of the oil extraction from soybean seeds (*Glycine max* (L.) Merr.). Presently, soybean hulls can be used as a fiber source for cattle, but they are also an excellent feedstock to produce nanocellulose. There are several studies to illustrate the nanocellulose production from soybean hulls. In one study, soybean hulls are first treated with cold alkali (17.5% NaOH), followed by hydrolysis using 1 M HCl at 80 °C for 2 h. The resulting pulp was then treated with a 2% NaOH solution, subsequently washed with deionized water, and then delaminated using the cryo-crushing method to create nanocellulose (Alemdar and Sain 2008; Ferrer *et al.* 2016). In a different approach, multistep reactive extrusion using 10% NaOH was adopted, followed by a 2-step treatment using 2% H_2SO_4 or alternatively bleaching with peracetic acid followed by a 1-step treatment using 2% H_2SO_4. Nanocellulose was produced by ultrasonification of the treated pulp (Debiagi *et al.* 2020). Soybean straw can also be used as a source for nanocellulose production. In two studies, soybean straw was suspended in 17.5% NaOH at room temperature for 15 h. After neutralization, the fibers were bleached with 4% H_2O_2/2% NaOH and then equilibrated in 2% H_2SO_4 at 90 °C for 3 h. The washed and dried fibers were then treated with an enzymatic cocktail (endoglucanase/xylanase) treatment, followed by mechanical defibrillation using an ultra turrax or ultrasonification (Martelli-Tosi *et al.* 2016, 2018.

OVERVIEW OF SCALABLE PROCESSING PROCEDURES FOR NANOCELLULOSE PRODUCTION WITH FOCUS ON PULPING

The processes used for pulping agro-based materials generally are the same as those used for pulping wood, although some notable differences should be considered. For example, to produce nanocellulose from fiber with a high content of elementary fibrils (as in some agricultural residues), the feedstock material can be treated with less energy-consuming approaches to achieve defibrillation. The demonstrated chemical pulping procedures to treat non-wood materials, including alkaline treatments (kraft, soda, soda-anthraquinone), acidic (sulfite, nitric acid), neutral sulfite (Rydholm 1965; Biermann 1993; Casey 1980; Rowell *et al.* 1997), and varying organosolv methods all indicated that they are effective in removing the lignin component. However, these approaches have not been optimized in terms of energy, costs, and the reduction of chemicals and water. Furthermore, several recent studies used milder pulping conditions to produce lignin-containing CNF (LCNF). Even though these fibers had lower crystallinity and not all lignin components were removed, the approaches used less pulping energy and fewer chemicals. The lignin presence within the cellulose fibers actually enhances its hydrophobic and thermal characteristics (Ewulonu *et al.* 2019; Najahi *et al.* 2022).

The procedures for pulping agricultural residues often start with a retting, dewaxing, or alkali pretreatment to swell the fibers and decrease the recalcitrance during pulping. Retting is a technique that uses moisture and microbes to break down or rot a lot of the plant's cellular tissues and pectin. This pretreatment also facilitates the separation of fiber from stem. The pulping approach for nanocellulose production from agro-plant residues can be divided into three types:

Alkaline Pulping Methods

These methods include (i) the kraft method using soda (A), soda/anthraquinone (AQ) followed by a bleaching treatment (mostly NaOCl to generate ClO_2, but occasionally H_2O_2); and (ii) the method of using 1 to 18 M KOH or NaOH, followed by a bleaching treatment. The above treatments can be applied in a reversed order, and in sequential stages. The adoption of the most appropriate alkaline treatment (i or ii) will depend on the feedstock properties. In the above methods, the alkali concentration can be mild (for dewaxing) or strong, and at different temperatures to achieve the stage of delignification. It can also be combined with anthraquinone catalysis (NaOH/AQ) since most non-woody plants do not need kraft pulping. Occasionally, researchers used mild acidic procedures instead of alkaline treatments to achieve pulping.

After pulping, the treated fibers are often subjected to bleaching, usually with acidic sodium hypochlorite ($NaClO$), sodium chlorite ($NaClO_2$), and occasionally H_2O_2, or a general bleaching sequence used for pulping of wood. Sometimes, strong alkali (usually in the range of 4 to 8 wt.% NaOH/KOH) is necessary to extract as much hemicellulose/pectin as possible from the plant. Otherwise, the pulp can be treated with weak acid by hydrolysis to remove hemicelluloses and pectin. These chemical treatments are multi-stage operations with appropriate washing steps, where they are well-developed procedures that date back to the 1940s.

Finally, the bleached pulp is defibrillated by different post treatments. For example, chemical (*e.g.*, TEMPO-mediated oxidation, carboxymethylation, phosphorylation, *etc.*) or enzyme treatments and be used to introduce surface charges on the cellulose surface to facilitate the defibrillation process (Sharma *et al.* 2020). This is because the presence of cellulose surface charge can induce electrostatic swelling and reduce the mechanical energy for delamination. Among the varying chemical treatments, TEMPO oxidation has been particularly noteworthy due to its effectiveness to create negatively charged carboxylate groups on the cellulose surface. The mechanical defibrillation process can be achieved by varying equipment as well as steam explosion treatment. None of the above methods have any upscaling issues regarding nanocellulose production from agricultural residues. Perhaps, this is because these methods are routinely used for wood pulping, such that they can be easily modified to treat agricultural residues.

The major concern of treating agricultural residues is that they typically contain a substantial amount of silica, which is accumulated in the epithelial cells of the plant (particularly grass) due to soil infusion during plant growth. The amount of silica in the plant can drastically vary, depending on the soil and environmental conditions, as well as the species itself. During alkaline treatment, silica can be dissolved, but the dissolved silica species can react with calcium ions, forming calcium silicates, which then have the potential to form scale on the walls of furnaces, boilers, superheaters, and evaporator tubes (Rowell *et al.* 1997). Currently, no viable solutions with satisfactory economics have been demonstrated to minimize the adverse effects of silica in alkaline pulping of agricultural residues. Additionally, the biological variability of agricultural residues is high, which often creates process control problems in modern alkaline pulping mills. Furthermore, there is a need for low-cost manufacturing methods to process agricultural residues, which indicates that the method should not involve an expensive recovery cycle.

Due to the above concerns, acidic pulping strategies (*i.e.*, sulfite pulping) may have some inherent advantages for processing agricultural residues with low lignin and high silica contents over alkaline pulping. When it comes to solvent pulping, the German pulp industry is an exception to the rest of the world. Germany has only sulfite mills but no kraft (sulfate) mills, as safety precautions have forbidden the installation of the Tomlinson-type recovery furnace in Germany due to the fear of kraft smelt-water explosions. Furthermore, Germany's strict environmental regulations ban obnoxious odors from the kraft process. However, the sulfite pulping process is more difficult, as it involves a complicated recovery cycle that is often not economically viable. The increased environmental and cost concerns, *i.e.*, without the use of sulfur and chlorine containing chemicals with a simpler pulping recovery procedure, have motivated the pulp industry worldwide to explore the organosolv pulping processes, as their recovery operations are considerably simpler and cheaper than those of traditional processes.

Organosolv Pulping Methods

A myriad of different pulping processes using varying organic solvents have been investigated over the years (Aziz and Sarkanen 1989; Hergert 1998; Johansson *et al.* 1987; Kleinert 1974; Paszner and Behera 1985; Stockburger 1993; Sundquist *et al.* 1988). There are several organosolv processes that have been the subject of major studies, including the AlCELL process, the Organocell process, the catalyzed (NEAM) alcohol organosolv pulping process, the alkaline sulfite-anthraquinone-methanol (Asam) process, the Acetosolv/Acetocell process, the Milox process, the Formacell process, and the Battelle-Geneva Phenol process.

The pioneering work on organosolv pulping processes dates to the 1930s, but it was not until the 50s, that extensive research began to identify an alternative to the kraft process. Initial efforts were mainly targeted to pulp wooden materials, with little research done to treat non-wooden materials. Usually, paper made from organosolv pulps exhibits slightly inferior properties than that made from kraft pulps, but this should not be a deterrent in the manufacturing of nanocellulose.

There are, however, a few known disadvantages with organosolv pulping that are well documented. (1) Organosolv pulping must be performed under an extremely tight and efficient control environment since any digester leaks cannot be tolerated due to the inherent fire and explosion hazards. (2) High pressure is often needed for delignification at higher temperatures, which poses additional risks. (3) Pulp washing is difficult during the exchange of solvent with an aqueous phase, whereas cumbersome pulp washing procedures are often employed. (4) There is also difficulty in using organosolv pulping to treat mixed plant species. Despite these challenges, the chemistry of organosolv pulping is well understood (McDonough 1993).

Not much is known, however, about how the high silicate content in the non-woody plant can affect the pulp quality and solvent regeneration capability. In terms of the economics of processing, the liquor-to-plant ratio is one of the most important operational variables, because this ratio directly affects the necessary capacity for solvent regeneration. Wood chips are relatively uniform in structure, but non-woody plants are not. Thus, some pre-preparation steps must be established for different feedstock materials to achieve a structure that is compatible with digester technology.

Selective organosolv processes are briefly described as follows. The Alcell (alcohol-cellulose) process (Williamson 1987; Koncel 1991; Pye and Lora 1991; Hergert 1998) probably represents the best commercial application, as demonstrated by continuous operations from 1985 to 1989. Historically, Kleinert (1974) was the first researcher who developed the ethanol-water pulping process. Nonetheless, the Alcell process displayed several problems. (1) The process did not involve the use of catalyst, and thus it was ineffective to pulp softwoods. (2) The high methanol content required the use of high-pressure reactors for delignification at temperatures between 190 to 200 °C, which increased the operational risks. (3) During the exchange of methanol to ethanol, the degree of polymerization in cellulose was found to decrease substantially. As a result, the process never truly became commercially viable. A variation of the Alcell process is the Neutral Alkali Earth Metal (NAEM) catalyzed alcohol pulping (Apulp) process (Paszner and Cho 1989; Paszner 1983).

The Organocell process (Dahlmann and Schroeter 1990; Stockburger 1993) is a solvent pulping process using NaOH, methanol, and catalytic amounts of anthraquinone as the pulping chemicals. The developer of this technology, Organocell GmbH, operated a 5 tonne/day pilot plant in Munich, Germany in the 80s. Organocell GmbH also started a full-scale operation of this process (150 ktonne/year) at the Bayerische Zellstoff mill in Kelheim in 1992. For various reasons, the upscaling of the process failed commercially, and this was a major setback for the advancement of organosolv processes in general.

Another interesting process is the Alkaline-Sulfite-Anthraquinone-Methanol (ASAM) process (Kordsachia and Patt 1987; Patt and Kordsachia 1986; Young and Akhtar 1997). This process has several advantages, but it does not meet the goal of a small scale, cheaper pulping procedures for processing non-woody materials. This process has, however, been successfully operated at the pilot-scale.

It was well known in the 40s that the acid catalyzed (sulfuric acid) acetic acid process could delignify wood. The process was investigated in greater depth by the Nimz group in Germany in the mid 80s and was labelled as the Acetosolv (or Acetocell) process (Nimz *et al.* 1989; Nimz and Casten 1986; Nimz *et al.* 1986). This process involves the use of 95% acetic acid with 0.1 to 0.2% HCl refluxed at 110 °C, which represents a mild delignification condition. Most of the work was conducted using wood as the feedstock, but the process has also proven viable for pulping non-woody plants, such as sugarcane bagasse, straw, elephant grass, and sunflower grass (Young and Akhtar 1997). The Acetosolv process was upscaled by the Veba Oil Company (Neumann and Balser 1993), but during the operation, severe material and corrosion problems occurred in the extraction equipment. As a result, this process has never been implemented on a larger industrial scale.

Instead of using acetic acid for delignification, many other acids such as formic acid and propionic acid have been investigated over the years. A particularly interesting combination is the combination of acetic acid with 5 to 10% formic acid, which was developed by Nimz and co-workers (the process is abbreviated as the Formacell process) (Nimz and Schoene 1993; Saake *et al.* 1995, 1998). This process offers the improved selectivity of delignification with higher pulp yields and represents a chlorine-free bleaching method. The Formacell process has been found to be effective to prepare non-woody pulps (Sundquist *et al.* 1988; Sundquist and Poppius-Levlin 1992; Seisto 1995; Lam *et al.* 2001; Vanderghem *et al*. 2012). However, this process has never been upscaled, so there is little information on the operational obstacles in upscaling and solvent recovery.

Another acid-based delignification is the oxidation of acids to their peroxy form. Finnish scientists have worked extensively on the use of peroxyformic acid and developed the Milox (Milieu Pure Oxidative) pulping process. They have evaluated this process in a pilot scale in 1992 to compare with a total chlorine free kraft mill. The oxidation of acids is an equilibrium process, but the rate of oxidation is slow and impractical for acids with two or more carbon atoms. Therefore, formic acid is the acid of choice in this process. The Milox process generally yields excellent fiber quality, but it also has some disadvantages, including the corrosive nature of formic acid, the need for zirconium coating of carbon steel, and the explosive nature of peroxides. The Milox process has also been used to delignify non-woody plants (Seisto 1995). At that time, there were few activities to manufacture nanocellulose from agricultural residues.

During the past decades, there has been a great deal of interest in biorefining, a method to fractionize biomaterials in their constituents. The goal generally is to make value-added materials out of them, such as bioethanol and other fuels. Extensive research efforts have been made in this field, but the economics have always been uncertain due to the low price of oil. As a result, many of the above-mentioned solvent pulping processes have been deemed not practical for large scale operations. Lignin can be extracted from both kraft and sulfite pulping, but carbohydrates are dissolved in hydroxy acids in kraft pulping and carbohydrates are oxidized to aldonic acid in sulfite pulping, so a simple valuation of carbohydrates, such as enzymatic treatment, is not feasible.

The solvent pulping process using sulfur dioxide-ethanol-water (40 to 65%) (SEW) (Schorning 1957; Westmoreland and Jefcoat 1991) has been supported by the American Process Inc. Researchers at Alto University (Herbert Sixta) and the University of Maine (Adriaan van Heiningen) and investigated quite extensively during the past decade. This process has several advantages. (1) The chemical recovery is simple in this process since SO_2 and ethanol can be recycled with low capital costs. (2) The process allows the rapid impregnation of the feedstock with ethanol, which is beneficial for rapid pulping and can handle heterogenous wood chips. (3) The process is suitable to treat the feedstock with a high ash content (Iakovlev and van Heiningen 2012a,b; Iakovlev *et al.* 2020a,b; Nelson *et al.* 2016). (4) The process can hydrolyze hemicellulose into monomers with minimum degradation. (5) The process can be applied to all lignocellulosic raw materials. As a result, SEW is useful to treat diverse agricultural residues, such as bamboo residues (Huang *et al.* 2018), OPEFB (Sklavounos *et al.* 2013) and sugar cane straw (You *et al.* 2017). The use of SEW to produce nanocellulose has been reported (Nelson and Retsina 2014; Nelson *et al.* 2016), but there are few details published due to proprietary reasons. There is a SEW pilot plant operated by the American Process Inc. at a capacity of 3 tonnes/day in Thomaston, GA, USA.

When evaluating the various pulping methods that may lead to the production of low-cost nanocellulose, nitro-oxidation process (NOP) turns out to be a highly unique method because (i) it can simultaneously delignify the feedstock and oxidize the cellulose scaffold and (ii) the processed effluent in NOP can be directly neutralized into a fertilizer, thus eliminating the solvent recovery need and offering the zero-waste feature. It is known that the usage of synthetic fertilizers in current farming practices creates a broken nutrient loop. Fertilizers are often over-applied, leading to excessive nitrogen leaching into water sources, and creating multiple water pollution problems. Furthermore, most of the nutrients from harvested food crops are left behind in agriculture residues, animal waste, and food waste. As NOP can extract all nutrients from organic feedstocks quickly and the effluent can be neutralized into effective fertilizers, the process has great potential to enhance the food-water nexus, close the nutrient loop, and offset the cost of nanocellulose production (due to its agricultural benefits). As a result, it was decided here to review this emerging and promising process in greater depth for low-cost nanocellulose production from lignocellulosic feedstocks using NOP. NOP can also offer the same cellulose oxidation features as TEMPO-mediated oxidation, such as controlled degree of oxidation, selective oxidation, facilitation of subsequent reactions, controlled derivatization, which are discussed below. However, the neutralization of NOP effluents, containing recovered nutrients and dissolved carbon fragments from the feedstock, into viable fertilizers will not be the subject for discussion here.

Nitro-Oxidation Process

In this section, two distinct functions of NOP will be highlighted: (1) delignification (pulping) of various plants, and (2) oxidation of cellulose. Both are essential to produce nanocellulose from untreated biomass feedstock. The delignification step is usually a rapid step, while the cellulose oxidation step is relatively slow.

Most early scientific work on cellulose oxidation was conducted by the group of Kenyon at Eastman-Kodak Research using cotton as the raw material, where the commercialization of bioabsorbable products started based on those studies (Unruh and

Kenyon 1942; Yackel and Kenyon 1942). As oxidized cellulose exhibited excellent hemostatic properties, Johnson and Johnson also entered the market with an oxidized knitted rayon fabric in the 1960s (Stilwell *et al.* 1998). Extensive research of these materials was later carried out in USSR, where a comprehensive review focused on the complex cellulose oxidation mechanisms using NOx was published in 1997 (Gert 1997).

For the pulping operation, there has been a large amount of work devoted to the use of nitric acid dating back to the 1860s. The early studies of this subject have been reviewed by Bolker (1966) and Rydholm (1965), where there are also more recent reviews available on its advances since then (Engström and Samuelson 1983; Singh 1990). Much of the early work was carried out in Germany. In practice, I. G. Farben operated a nitric acid mill in Wolfen during the second world war and produced dissolving pulp in the 50s. (Beazley 1957; Rydholm 1965). The idea of using the spent liquor as a fertilizer was also investigated by Brink (Brink 1961a,b, 1962). The above reviews gave extensive details of the studies prior to 1962 and discussed various upscaling issues. It was also found that ammonia can be used instead of sodium hydroxide for the extraction of nitrolignin (Bolker 1966). As the spent liquor from nitric acid pulping contains considerable amounts of nitrogen content, it can be neutralized to produce fertilizer with normal activity (Brink 1961a,b, 1962). The Brink paper focused on the process of nitric acid pulping but not cellulose oxidation, where the latter is essential for making nanocellulose. Later, Brink also developed the NOx/O_2-technology (NOx includes NO_2, N_2O_4 and N_2O_3) and patented this process (Brink 1978), which was later extensively investigated by Olle Samuelsson at Chalmers University in conjunction with MoDo and Valmet, where many patents were filed (Samuelson 1983a, 1984, 1986, 1989, 1990). The process was called PRENOX, which was successfully tested in pilot-scale but was never commercialized.

Nitric acid as pulping agent and an oxidant

Nitric acid is a strong acid and a potent oxidant, but the disadvantage is that it frequently breaks carbon-carbon bonds, resulting in low degrees of polymerization (DP) of the cellulose chains. The specificity of the oxidation can, however, be enhanced using nitrogen dioxide (NO_2) instead of nitric acid (Unruh and Kenyon 1942; Yackel and Kenyon 1942). This is because NO_2 easily dissolves in cold water with subsequent formation of nitrous and nitric acids (Gajdziok and Vetchý 2015),

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (1)$$

where nitrous acid will subsequently be converted to nitric acid:

$$3HNO_2 \rightarrow HNO_3 + NO + H_2O \qquad (2)$$

It has been suggested that nitric acid will be present in any nitrogen tetroxide scheme for cellulose oxidation and that oxidation goes through a nitration stage (McGee 1947a,b):

$$2N_2O_4 + H_2O \rightarrow 2HNO_3 + N_2O_3 \qquad (3)$$

$$(C_6H_{10}O_5)_x + xHNO_3 \rightarrow (C_6H_9ONO_2)_x + xH_2O \qquad (4)$$

$$N_2O_4 + (C_6H_9ONO_2)_x \rightarrow (C_5H_8\ COOH)_x \qquad (5)$$

Hence, the presence of nitric acid together with nitrogen tetroxide can result in rapid denitration-carboxylation. Nonetheless, the majority of hypotheses operate under the presumption that cellulose nitrites are produced as an oxidation byproduct of the process

(Gert 1997). Moisture is an essential prerequisite for effective oxidation. A moisture concentration of roughly 5.5 to 11% (w/w) is required in the input cellulose material for the adsorption of dimeric nitrogen oxide. When the moisture level is low, the reaction just nitrates the cellulose. The grade of cellulose oxidation is determined by the amount of absorbed N_2O_4, which is indirectly proportional to temperature.

The oxidation of cellulose with NOx is primarily targeting the oxidation of C6 hydroxyl groups (Nevell 1951; Gal´braikh 1971; Yasnitskil 1971), but it was also understood that the C2 and C3 hydroxyl groups can be oxidized into aldehyde and ketone groups in a complex manner. The mechanism of the nitro-oxidation of cellulose has been studied by many researchers. The early investigators proposed a route that the intermediate formation can be achieved by the formation of cellulose nitrate (McGee 1947b; Yackel and Kenyon 1942). Later it was revised that cellulose nitrate is formed first, but it can be decomposed by a radical mechanism (Pavlyuchenko 1958). This hypothesis was further refined that with subsequent stabilization of the radical, the process can yield oxidized cellulose (Stakheeva-Kaverzneva 1959). In oxidized cellulose, the C6 carboxyl groups constitute about 85% of the total carboxyl group content (determined by the Lefévre-Tollen method using uronic acid). This implies that the side reactions in this process produce other functional groups instead of carboxyl groups in the C2-C3 position. These other functional groups include aldehyde and ketone groups, which are formed due to the instability of oxidized cellulose in weak alkali. The nitrogen content of the oxidized cellulose is generally small, ranging between 0.05 and 0.25 wt%. Oxidized cellulose produced in these studies also showed signs of instability during storage, even under dark conditions (so their properties should be measured as soon after their preparation as possible). It was found that oxidized cellulose displayed high copper number (characteristic of aldehyde functions), which is generally correlated with the carboxyl group content. However, it is well known that there is no stoichiometric relationship between a carboxyl cellulose's aldehyde concentration and its copper number. Astonishingly, the oxidation of cellulose with NOx was found not to be sensitive to the moisture content between 0 to 18% moisture, when oxidation was run for a long time (*e.g.*, 8 days). (Yackel and Kenyon 1942). It is thus important to note that the effect of water is different for cellulose oxidation using nitric acid when compared with the pulping (delignification) process using nitric acid as discussed by the Brink patent. It can be emphasized that cellulose with different degrees of oxidation is vital for different types of applications, where the degree of oxidation can be controlled by the chosen oxidizing treatment conditions. The charged groups on the cellulose chains created by the moderate acid treatments, oxidative treatments (*e.g.*, TEMPO-mediated oxidation, periodate-chlorite oxidation, nitro-oxidation), or enzymatic hydrolysis, can be carefully controlled by the reaction conditions. The feasibility of these treatments at large-scale commercial scale to produce nanocellulose is completely within our reach (Das *et al.* 2022)

Possible reactions during nitric acid/nitrogen dioxide pulping

During nitric acid/nitrogen dioxide pulping, nitrous acid (HNO_2, formed when nitric acid contacts with water) was early found to be the most reactive species in the process (Varela 2003). Pigman *et al.* (1949) first suggested that nitrous acid acts as the major oxidative species in this process, although Arendt *et al.* (1973) later suggested that it is nitrosonium ions (NO^+) instead of nitrous acid that functions as the major oxidative species (Arendt *et al.* 1973).

When NOx is in contact with water, it creates nitric and nitrous acid similar to when nitric acid and nitrites are used in the recently demonstrated NOP route (Pigman *et al.* 1949):

$$HNO_3 + NaNO_2 \rightarrow HNO_2 + NaNO_3 \qquad (6)$$

Hence, nitrous acid can be formed both from NOx and nitric acid/nitrite. In general, with nitrogen dioxide, all of the different substitution, side chain cleavage, and oxidation reactions seen with nitric acid are likely to happen. In addition, the free-radical reactions, involving the addition of nitrogen dioxide to the aromatic ring in lignin, hydrogen abstraction and electron transfer from phenolic groups may also take place. The role of free radical still needs to be clarified, but some recent papers on features of stable radical generation in lignin on exposure to nitrogen dioxide are summarizing the state of knowledge (Singh 1990). The EPR (electron paramagnetic resonance) method has been used to identify the generation of phenoxyl, iminoxyl, and acylaminoxyl radicals. The primary oxidative interaction of phenol groups with dimers of NO_2 (nitrosyl nitrate) results in the generation of phenoxyl radicals and nitric oxide, according to the hypothesized mechanism (Davydov *et al.* 2013; Gaponova *et al.* 2010; Gaponova *et al.* 2018)

Obviously, the lignin reactions occurring during nitric acid pulping are very complex. The reactions involved during pulping are rapid electrophilic substitution of the aromatic nuclei of lignin with nitro-groups, as would occur in similar treatments of phenol or phenolic ether groups. At those phenylpropane monomers containing a free phenolic hydroxyl, substitution will occur in the 5-position, whereas in etherified monomers, the primary substitution is likely to be in the 6-position. Further nitration brings about scission of the side chain and nitration in the 1-position, and also hydrolysis of the phenolic ether bonds to pyrocathecol configurations, which are rapidly oxidized into quinones. The group of Samuelson and coworkers have suggested that demethylation and nitration are important first reactions. However, some researchers did not support the assumption that demythylation reaction is the first reaction (Ohi and McDonough 1992), which was disputed by another research group (Sobolev 1961). There are a multitude of reaction products from lignin, including CO_2, CO, N_2, N_2O, NO, NO_2, CH_3OH, carboxyl groups, nitration of lignin (Abrahamsson *et al.* 1981; Anderssan and Samuelson 1985; Andersson *et al.* 1984; Rasmusson 1989; Rasmusson *et al.* 1987; Rydholm 1965). The exact mechanisms are, however, not yet completely understood. A simplified reaction scheme for nitric acid pulping is given in Fig. 4.

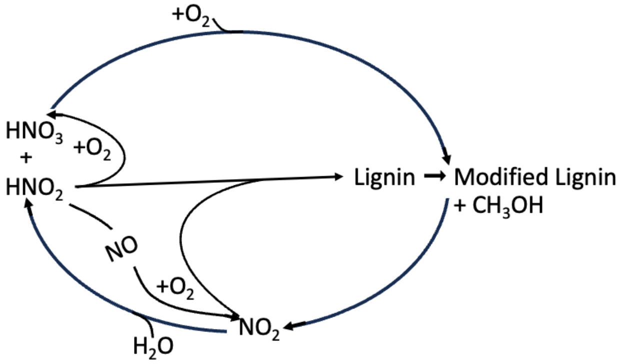

Fig. 4. A simplified reaction scheme of nitric acid pulping (delignification) (Figure is redrawn according to Engström and Samuelson 1983)

In this scheme, the creation of NO, generally an inert species, in the presence of oxygen, can be oxidized into NO_2 (approximately 30 mole% NO can be converted to NO_2) (Abrahamsson *et al.* 1981). Another important aspect shown in Fig. 4, is autocatalytic reactions involving inorganic nitrogen compounds of oxidation state +2 to +5, which are key reactions when kraft pulps are brought into contact with NO_2 (Engström and Samuelson 1983; Rasmusson and Samuelson 1986; Rasmusson *et al.* 1987; Samuelson and Ojteg 1990, 1991; Rasrnusson and Samuelson 1993). In several studies, the treatment of wood pulp with NOx with excess oxygen permits an extensive oxidation of lignin (Abrahamsson and Samuelson 1984) without incurring significant oxidative depolymerization of carbohydrates (Andersson and Samuelson 1983). This leads to improved delignification and reduced depolymerization of carbohydrates after subsequent bleaching (Andersson and Samuelson 1983; Samuelson 1983b). There have been different strategies reported for the optimization of bleaching. In one study, the process starts with the addition of NOx at medium to high pulp consistency (10 to 25%), followed by dilution of $NaNO_3$ mixed with a smaller amount of HNO_3 (at lower temperature) to a consistency around 5%, then subjected to a high temperature treatment at 80 to 90 °C (referred as ripening). After these treatments, the pulp is treated with alkaline oxygen bleaching (Rasmusson and Samuelson 1990; Rasrnusson and Sarnuelson 1993; Samuelson and Ojteg 1996; Samuelson and Ojteg 1987). The alkali treatment after bleaching is due to the necessity to extract residual lignin (Larsson and Samuelson 1990; Larsson and Samuelson 1991).

NOx will promote the reduction of sugar and formation of aldonic end groups on cellulose and hemicellulose chains. The reduction of sugar end groups should promote depolymerization; however this reaction cannot explain why retarded depolymerization was observed (Andersson and Samuelson 1983). The Samuelson group showed that it was the modification of lignin during the NOx pretreatment that is responsible for the lower rate of depolymerization of cellulose chains. This modification was thought to suppress active intermediates that promote reactions to depolymerize the carbohydrates. The generation of NOx was also found to be a prerequisite for extensive delignification without a serious attack on the cellulose chains (Samuelson and Ojteg 1990). The influence of the consistency during peroxidation of kraft pulp with NOx/O_2 has also been investigated. A high consistency was found to increase delignification and selectivity (Basta and Samuelson 1984; Samuelson 1985; Samuelson and Sjoeberg 1983). In another study, it was reported that that a peroxidation at medium consistency (10 to 15%) is most suitable for industrial applications (Samuelson and Oejteg 1985).

There are also several pulping studies involving the use of HNO_3. For example, there is a low concentration HNO_3 pulping treatment demonstrated (Rydholm 1965), which is probably more effective for biomass with lower lignin content. In a different study, bagasse feedstock was first treated with 15% HNO_3 and then with 8% NaOH to produce a delignified bagasse pulp (El-Taraboulsi *et al.* 1983). In an issued patent, the pulping treatment can be accelerated using HNO_3 under the presence of aluminum salts (Prior 1987). Unfortunately, the mechanistic role of such salts is unclear. In another study, it was found that the single-stage nitric acid treatment at higher temperature (70 ºC with 55% HNO_3) was able oxidize the cellulose, with resulting pulp properties similar to those from the two-stage treatment (*i.e.*, the primary pulping stage using nitric acid and the secondary oxidation stage using sodium nitrite) (Gert *et al*. 1995). Finally, the PRENOX consortium has also reported pilot trials at the Östrand mill in Sweden. These reports have probably less current importance but showed that upscaling of nitro-oxidation process is feasible

(Lindqvist 1985, 1986; Brännland 1986, 1991; Simonsson 1986, 1987b, 1991; Brännland *et al.* 1990a,b; Simonson *et al.* 1987a).

Advances of Nitro-Oxidation Process to Produce Nanocellulose for Water Remediation Using Agricultural Waste and Natural Fibers as Feedstocks

The nitro-oxidation process is of great interest for commercial production of large-scale nanocellulose materials for varying industrial applications, including energy storage, drug delivery, tissue engineering, wound healing, packaging, drilling, coatings, construction (cement), cosmetics, and water purification. With low-cost nanocellulose, there will be many new economic opportunities for these applications. However, among them, the need of low-cost nanocellulose for water purification in rural communities, perhaps is the most urgent one in our society (Das *et al.* 2022). This is because ensuring safe drinking water a fundamental human right. The production of potable water using low-cost but environmentally friendly materials or technology is very challenging. Many of the existing water purification methods are not sustainable because of their dependency on synthetic materials that are relatively expensive and not biodegradable. Low-cost production of nanocellulose from underutilized agricultural waste or natural fibres may overcome this challenge. As a result, it was decided to only highlight this subject in this review, as using low-cost nanocellulose for sustainable clean water production may offer the greatest societal impact.

In addition to the low-cost potential of the feedstock, non-woody agricultural residues and natural fibers can offer some unique composition and structure features (*i.e.*, low lignin content and porous cell wall structure), thus facilitating the pulping/defibrillation process. These feedstocks are particularly suited for the NOP approach to produce nanocellulose materials for a variety of water remediation treatments (Das *et al.* 2022). The varying applications of using nanocellulose extracted from agricultural waste and natural fibers (*e.g.*, jute, spinifex grass, bamboo, moringa and sorghum stalk) using NOP approach have been the focus of the authors' laboratory over the last few years (Sharma *et al.* 2017a,b; 2018a,b, 2018c). For example, cellulose nanofibers extracted by NOP (NOCNF) using Australian spinifex grass as a feedstock exhibited a very high Cd(II) removal efficiency (the maximum adsorption capacity of NOCNF toward Cd(II) ions in water was about 2550 mg/g), where the adsorption time was also very short (within 5 min) (Sharma *et al.* 2018a). Another study demonstrated that NOCNF extracted from Jute effectively removed UO_2^{2+} ions (the maximum adsorption capacity of NOCNF ~ 1250 mg/g) as well as for Pb(II) ions (maximum adsorption capacity of NOCNF ~ 2270 mg/g) from water (Sharma *et al.* 2017a, 2018b). The removal mechanisms involved the synergistic events of electrostatic interaction (metal ion adsorption on NOCNF - nucleation) and mineralization (metal hydroxide nanocrystal growth on NOCNF). Besides the NOP method, a recent study using the sulfuric acid hydrolysis approach to produce nanocellulose from pineapple leaves found the nanocellulose/polyurethane composite exhibited good dye adsorption properties. Furthermore, this composite showed high selectivity towards rhodamine B (271 mg/g) over methylene blue (Chandrashekhar *et al.* 2020).

Thus far, nanocellulose-based adsorbents prepared by different approaches to remove a wide range of charged contaminants, such as dyes, heavy metals ions and pharmaceuticals, are the most investigated subject (Das *et al.* 2022; Sharma *et al.* 2022). For practical applications, some challenges exist when solely depending on the adsorption approach, which include the entrapment capacity of the system, the flow characteristics of the contaminant stream, and the recycling of the adsorbed materials. For this purpose, a new class of nanocellulose-based thin-film nanofibrous composite membranes (TFNC) was developed by the research group, aiming to overcome these problems (Ma *et al*. 2011). The TFNC membranes contain multilayered fibrous cellulosic scaffolds that consist of charged surface and fibers with diameters from nanometers to microns. The top nanocellulose barrier layer enables the system to possess both adsorption and filtration properties. Some unique advantages of such TFNC membranes include the fouling reduction tendency, biodegradability and potential low-cost (Joshi *et al.* 2023; Sharma *et al.* 2020; Yang *et al.* 2021; Yang *et al.* 2022).

CONCLUSIONS

Truly abundant and diverse underutilized non-woody biomass sources, such as agricultural residues and natural fibers, can be used as sustainable feedstocks for production of high value nanocellulose materials. As many non-woody plants have loose structure and low lignin content, relatively simple pulping and chemical treatments can be used for nanocellulose production. This review has summarized the typical pulping and oxidation treatments used for production of nanocellulose from a variety of agricultural residues and natural fibers, where some treatments can be even more simplified to reduce the consumption of chemicals, energy and water. The adoption of low-cost processes for pulping and cellulose oxidation treatments, such as alkaline, solvent pulping, and nitrogen-oxidation treatments to covert high value nanocellulose (CNF/CNC) from low value non-woody biomass can create new opportunities to achieve greater sustainability in biobased economy. The nitro-oxidation process is a particularly interesting pathway, as the processed effluent can be neutralized directly into a fertilizer, thus generating no waste in the process. As a result, this process has great potential to produce low-cost nanocellulose as it can offset the production cost with agricultural benefits.

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DECLARATION OF COMPETING INTEREST

B.S.H. holds equity and serves as a board of director for SWFT Labs, Inc. Although a financial conflict of interest was identified for management based on the overall scope of the NSF-PFI-TT-2140820 project and its potential benefit to SWFT Labs, the research findings included in this work may not necessarily related to the interests of SWFT Labs. The terms of this arrangement have been reviewed and approved by Stony Brook University in accordance with its policy on objectivity in research.

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