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Review

Review on Nonconventional Fibrillation Methods of Producing Cellulose Nanofibrils and Their Applications

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Cite This: *Biomacromolecules* 2021, 22, 4037−4059

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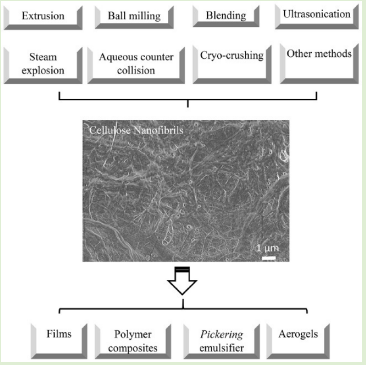
ABSTRACT: The production of cellulose nanofibrils (CNFs) continues to receive considerable attention because of their desirable material characteristics for a variety of consumer applications. There are, however, challenges that remain in transitioning CNFs from research to widespread adoption in the industrial sectors, including production cost and material performance. This Review covers CNFs produced from nonconventional fibrillation methods as a potential alternative solution. Pretreating biomass by biological, chemical, mechanical, or physical means can render plant feedstocks more facile for processing and thus lower energy requirements to produce CNFs. CNFs from nonconventional fibrillation methods have been investigated for various applications, including films, composites, aerogels, and *Pickering* emulsifiers. Continued research is needed to develop protocols to standardize the characterization (e.g., degree of fibrillation) of the lignocellulosic fibrillation processes and resulting CNF products to make them more attractive to the industry for specific product applications.



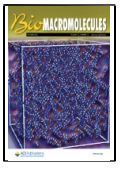
1. INTRODUCTION

The production of nanocellulose is an extensively investigated area. Nanocellulose can be produced chemically, physically, mechanically, or biologically. Mechanical methods are commonly used for producing cellulose nanofibrils (CNFs). In a previous review, mechanical fibrillation methods were grouped into conventional and nonconventional methods.[1] Conventional fibrillation techniques, including homogenizing, grinding and refining, have proven effective in producing CNFs and have been scaled up to an industrial production level.[2,3] There are, however, limitations to such methodologies, including high energy consumption, low production efficiencies (low solid content), and high cost of final products.[4] Therefore, various types of nonconventional fibrillation methods for producing CNFs have emerged and are becoming increasingly important. In the current work, we summarize the recent progress in developing nonconventional fibrillation methods, including extrusion, ball-milling, blending, steam explosion, aqueous counter collision, ultrasonication, cryogenic crushing (cryocrushing), and others. Methods to characterize the degree of fibrillation, and a review of pretreatment methods employed are also presented. Finally, an overview of the current fields of application of CNFs is given. To the best of our knowledge, there has been no review article primarily focused on nonconventional methods of producing nanocellulose. This article is intended to fill that knowledge gap.

1.1. Nanocellulose.

A nanomaterial is a material with at least one dimension on the nanometer scale. By reducing the size of a common cellulose fiber (tens of microns in diameter), nanocellulose can be produced. The two common methodologies to produce nanocellulose from wood or plant cell walls follow either a chemical or mechanical route. The production of nanocellulose from plant cell walls goes back to 1950s when Rånby explored the colloidal properties of cellulose micelles from mercerized pulp.[11] In the 1980s, Turbak et al. used high pressure homogenization of cellulose pulps to produce cellulose microfibrils (CMFs) (Figure 1a), which comprised fibrils with diameters ranging from 25 to 100 nm.[12] Since then, significant research efforts on the production and use of nanocellulose have occurred. Nanocellulose can be produced in a bottom-up approach using bacteria, generating bacterial cellulose (BC) (Figure 1b).[6] Most chemically produced nanocellulose uses acid hydrolysis to liberate the nanoscale, crystalline portions of the plant cell wall, which are referred to as cellulose nanocrystals (CNCs) (Figure 1c).[13] CNCs typically have uniform sizes ranging from 100 to 200 nm in

Received: May 20, 2021
Revised: August 24, 2021
Published: September 10, 2021



https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

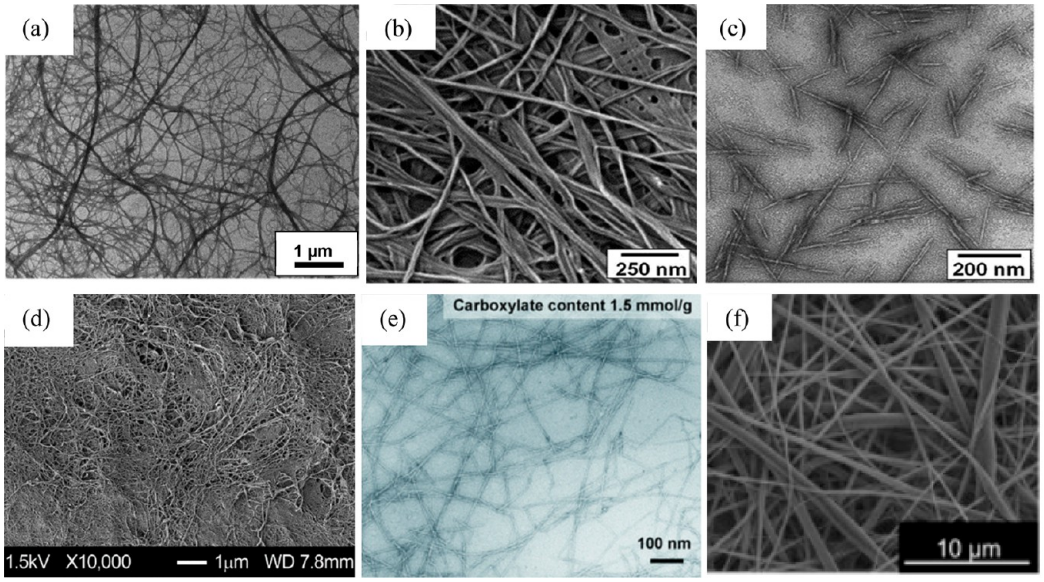


Figure 1. Various types of nanocellulose. (a) Transmission electron microscopy (TEM) graph of cellulose microfibrils (CMFs). Adapted from ref 5 with permission. Copyright 1997 Wiley-VCH. (b) Scanning electron microscopy (SEM) graph of bacterial cellulose (BC). Adapted from ref 6 with permission. Copyright 2007 American Chemical Society. (c) TEM graph of cellulose nanocrystals (CNCs). Republished with permission of Royal Society of Chemistry, from ref 7; permission conveyed through Copyright Clearance Center, Inc. (d) SEM graph of cellulose nanofibrils (CNFs). Adapted from ref 8 with permission. Copyright 2009 Wiley-VCH. (e) TEM graph of TEMPO-mediated cellulose nanofibers (TOCN). Adapted from ref 9 with permission. Copyright 2007 American Chemical Society. (f) SEM graph of electrospun cellulose nanofibers (ECNFs). Reprinted from ref 10. Copyright 2019 with permission from Elsevier.

length and 10 to 30 nm in diameter. Alternatively, mechanically produced nanocellulose typically employs some form of grinding or shearing of pulp fibers in aqueous suspensions to reduce fiber dimension; equipment such as disc refiners or stone grinders (super mass colloider) are commonly utilized in such operations.[14] These mechanically derived, nanofibrillated cellulose materials, termed "cellulose nanofibrils" (CNFs), have hierarchical structures comprising interconnected fibrils ranging from submicron to tens of microns in length, with diameters ranging from several nanometers to several microns (Figure 1d). Because of this multiscale dimensionality, mechanically derived nanocellulose is challenging to process and characterize. Significant research efforts have combined chemical and mechanical means to produce nanocellulose, with the most researched technique being the production of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibers (TOCN) (Figure 1e).[15] Considering the chemical method (TEMPO), rather than the mechanical method (ultrasonication), as the primary force for fibrillating, TOCN will not be covered in this paper. Another category of nanocellulose generated from nonconventional methods is electrospun cellulose nanofibers (ECNFs) (Figure 1f).[16] Since ECNFs are not obtained through fibrillation, they will not be included in the current review. The scope of this Review covers nonconventional fibrillation methods for producing nanocellulose fibrils (mainly CNFs and CMFs), including mechanical and physical approaches.

1.2. Limitations of Conventional Fibrillation Methods for CNFs. CNFs are typically produced by three conventional processes: homogenization (including microfluidizing), grinding, and refining.[1] A brief explanation of the working principles of these three methods follows. During homogenization, cellulose fiber suspensions flow through extremely small gaps between an impact ring and a valve under intensive shear, which reduces the fiber into nanofibrils. Similar in principle, a microfluidizer is constructed with a chamber containing either a *Z*- or *Y*-shape channel. Such a channel enables cellulose fibers to intensively interact with the inside of the microfluidizer's chamber, resulting in significant size reduction of the fibers. To produce the high shear forces required within the microfluidizer, the channel size is very small. The limited channel size relative to large fiber dimensions can result in fiber clogging during microfluidizing.[17] A grinder consists of a stationary disk and a rotational disk, generating shear force during operation. By controlling the gap between the stationary and rotational disks, as well as rotational speed and material flow rate, high shear conditions can be applied to cellulose fibers to fibrillate them into nanofibers. Disk refining is very similar to grinding in terms of the fibrillation mechanism and differs only in that the gap size is greater in disk refining. As a result, the fibrillated fibers from the disk refining process vary largely in fiber dimensions, ranging from micron to nanoscale. As such, the product from disk refining is often referred to as CMFs. Disk refining is commonly used as a mechanical pretreatment for manufacturing more consistent CNFs.

Conventional fibrillation methods are energy intensive, with typical energy consumption around 20 kWh/kg for homogenizing,[17] 4−15 kWh/kg for grinding,[3,17−19] and 3−6 kWh/kg for microfluidizing.[17,20] The estimated price of CNFs produced from homogenization ranges from $2 to $200/kg, depending on the pretreatment type.[21] Producing CNFs with less energy is one of the driving forces for the development of nonconventional fibrillation methods. For example, the energy consumption during twin-screw extrusion (TSE) fibrillation of biomass has been reported to be in the range of 2−6 kWh/kg, most of which involved the use of chemical/enzymatic pretreatments before fibrillation.[18,19,22−24] However, some nonconventional fibrillation methods have high energy demand, that is, 40−48 kWh/kg for sonication,[25] 10−15

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

kWh/kg for blending[26,27] and 15 kWh/kg for aqueous counter collision.[28]

Another limitation of CNFs produced from conventional fibrillation methods is their low solids contents (<5 wt %) in aqueous suspensions.[1] These methods require processing at low solids contents to prevent the cellulose fiber suspension from becoming too viscous for feeding and fibrillation.[1] The low solids content of CNF suspensions negatively impacts their economics by increasing the transportation cost (on a mass basis) and requiring subsequent compacting and dewatering.

2. DEGREE OF FIBRILLATION

There are a range of tools for characterization of various attributes of CNFs. While the majority of these characterization methods are widely accepted, there remains unresolved challenges, particularly relating to quantification of the "degree of fibrillation". Two factors in particular should be considered with regard to characterization of fibrillation. First, the number or percentage of nanofibrils under a certain threshold diameter, as well as the average aspect ratio of the resulting fibrils, is typically reported. This quantity is commonly referred to as the "fines level" of the material.[29] Second, few authors make the distinction between internal and external fibrillation, meaning the complete isolation of individual nanofibrils versus those that are still partially affixed to larger fiber bundles. The relative amounts of each should be considered when reporting the fibrillation extent resulting from a given processing technique.[29,30] The following sections discuss how "degree of fibrillation" is commonly measured and reported.

2.1. Direct Measurements. Currently the only direct method of measuring the size of CNFs is through visual observation via one of several microscopy techniques. Such methods include optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and fluorescence microscopy.[22,31,32] SEM and TEM in particular are widely used by researchers to measure the dimensions of nanofibrils on a range of scales. Measurements are relatively straightforward, as two-dimensional images are obtained, and the fibrils' lengths, diameters, and aspect ratios can be measured either manually, or via image analysis software.[33−37] However, the electron microscopic methods only focus on a very small area of materials. So the results from such characterizations are unlikely representative of the whole materials.

2.2. Indirect Measurements. The remainder of the characterization techniques commonly employed to assess the quality of CNFs are indirect measurements. In these measurements, a property is measured which provides a qualitative estimate of fibrillation based upon a known relationship between the measured parameter and the CNF size/degree of fibrillation. The relationship itself is often determined using additional characterization techniques and it is assumed applies uniformly across samples. Indirect measurements of CNF fibrillation are often performed using cellulose suspensions in water or other solvents at a range of concentrations.

2.2.1. Viscosity. As the degree of fibrillation increases during processing, the size of the fibrils generally decreases. Creating smaller or more highly fibrillated CNFs progressively increases fibril−fibril interactions, resulting in greater suspension viscosity.[29,38−40] Therefore, researchers have used viscosity to qualitatively determine the degree of CNF fibrillation. Attempts have been made to fit models to viscoelastic data to gain a more quantitative correlation between the extent of CNF fibrillation and suspension viscosity.[22,41] To date, no widely accepted quantitative relationship between viscoelastic data and CNF dimensions/degree of fibrillation has been established.

2.2.2. Transmittance and Turbidity. The transmittance of light through a suspension is related to the particle or fibril dimensions, surface area and interparticle interactions at a given concentration. A higher transmittance generally correlates to a more highly fibrillated material. The turbidity of a suspension is a measurement of the light scattered at 90° to the incident light. The turbidity is a function of the number, shape, and size distribution of scatterers in a suspension, as well as the refractive indices of the scatterers and the suspension medium. Similar to transmittance, the turbidity of a suspension can be used to qualitatively assess the fibrillation of CNFs, but results are also affected by any agglomeration of fibrils in the sample.[4,40] Transmittance or absorbance, and turbidity values are most commonly measured using an ultraviolet−visible (UV−vis) spectrophotometer. Recently, more specialized and automated equipment has become available that combines transmittance measurements with optical image analyses of residual microscale fibers after fibrillation to provide an estimation of the degree of fibrillation.[30,38,40]

2.2.3. Dynamic Light Scattering (DLS). DLS measures particle size in solutions or suspensions, and makes the assumption that all particles are spherical. DLS uses time-dependent fluctuations of the intensity of light scattered by particles in solution undergoing Brownian motion. These fluctuations are related to the hydrodynamic radius of the particles (assuming they are spherical), which have a constant diffusion coefficient in all directions. Because of their high-aspect ratio, many conformations, and tendency to agglomerate, CNFs are challenging to characterize via this method.[40,42]

2.2.4. Water Retention Value (WRV). WRV is a widely used index in the pulp and paper industry to assess the degree of fibrillation of a sample via the amount of water retained under specific conditions.[22,37,43] The higher the WRV, meaning the greater the amount of water retained by fibrils, the higher the degree of fibrillation. The method was developed for use with pulp fibers with diameters on the tens of microns. Researchers have however employed centrifugation to measure the WRV of micro- or nanofibrils via the reduction of easy-to-remove bulk water, leaving water bound to fibril surfaces and in their pores.[22,44] Similarly, the Canadian Standard Freeness (CSF) measures the water drainage rate from fibers and is often correlated to a degree of fibrillation, as the CSF value is related to the surface area and swelling behavior of fibers and fibrils. Like the WRV, CSF is primarily used for larger fibers, and its efficacy with micro- and nanomaterials is problematic, as the drainage rate is reduced to near-zero as the fibril size decreases.[37]

2.2.5. Specific Surface Area. The surface area of CNFs can be used to estimate the degree of fibrillation since the surface area of fibers increases substantially when they are disaggregated into fibrils. It is noted however that a surface area measurement gives little, if any, indication of the length or aspect ratio of the fibrils or information regarding the extent of internal versus external fibrillation. Furthermore, surface area measurements of CNF are often difficult to interpret. Most surface area measurements rely upon the adsorption of a probe species onto the fibril surface (common probe species include

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

water, gas, dyes, charged species, and enzymes).[45,46] Clearly, the physical size of the probe molecule, and it propensity to adsorb, must be considered when evaluating the efficacy of a surface measurement technique as applied to cellulose fibrils.[22,29,46] UV−vis spectroscopy, coupled with a dyeing procedure and subsequent centrifugation, is commonly used to measure specific surface area of CNFs.[46] Additional adsorption-based methods for measuring the surface area of CNFs include Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) analyses employing nitrogen gas adsorption and desorption.[29,43]

2.2.6. Quality Index. Since it is almost impossible to characterize the degree of fibrillation of CNFs with a single method unbiasedly, a multifactor "Quality Index" (Q.I.) was proposed.[4] The classic Q.I. has eight factors: nanosized fraction, turbidity, Young's modulus, porosity, transmittance at 550 nm, tear resistance, macrosize, and homogeneity. A simplified Q.I. was found to give similar results as the classic Q.I. did, with less parameters. The calculation of Q.I. is listed in eq 1.

$$\text{Q.I.} = 0.3x_1 - 0.03x_2 - 0.072x_3^2 + 2.54x_3 - 5.34\ln(x_4) + 58.62 \quad (1)$$

where x_1 = nanosized fraction [%], x_2 = turbidity [NTU], x_3 = Young's modulus [GPa], x_4 = average macro size [μm^2] of the fibers measured using ImageJ software and optical microscopy images. The Q.I. was reported to be sensitive to the changes in the energy consumption during fibrillation, pretreatment type/level, drying method, hemicellulose content and pre-refining. The Q.I. was considered important in three ways: (1) providing an easy tool for CNF quality control and process optimization at both lab and industrial scale production, (2) potentially linking energy consumption to CNF quality, and (3) benchmarking various CNF products and guiding their applications.

3. BIOMASS PRETREATMENTS

Many researchers have invested significant effort in the development of pretreatments that potentially reduce the energy consumption for CNF production and ensure consistency of the products' composition and properties.[47] Additionally, pretreatments have been shown to reduce the likelihood of clogging during the disintegration process.[44] Different strategies have been developed for the pretreatment of lignocellulosic feedstocks for CNF production. Such strategies include chemical,[48−51] physical,[52,53] mechanical,[54,55] and enzymatic treatments,[56,57] in addition to combinations thereof.[18,58] The pretreatment of lignocellulosic materials for CNF production via conventional fibrillation processes is well understood and has been reviewed in previous publications.[1,14] In this section, we will focus on pretreatments used for nonconventional fibrillation processes, including extrusion, milling, blending, and aqueous counter collision.

3.1. Chemical Pretreatments. Chemical pretreatments have been applied to lignocellulosic materials to remove lignin, hemicellulose, pectin, etc., introduce specific functional groups and to reduce the energy requirements for fibrillation. Alkaline treatments are widely used for pretreatment of feedstocks for CNF production. Often, an alkaline treatment is coupled with a bleaching process, commonly employing sodium chlorite ($NaClO_2$), to further remove lignin residues. For instance, Chaker et al. applied a NaOH treatment (5 wt %) at 80 °C for delignification and followed by bleaching with $NaClO_2$.[48] They compared the efficiency to a delignification process which only used $NaClO_2$. Their results suggested that, while the cellulose content of the treated fiber increased for both methods, NaOH-treated fibers had the highest cellulose content.

Oxidative pretreatments are another important strategy for the production of high-quality CNFs with reduced energy consumption.[47,59] Through the oxidation process, carboxylate and aldehyde functional groups are introduced onto native cellulose fibers. The negative charges increase the repulsion between fibers and aid in the defibrillation process. During TEMPO oxidation of CNFs, NaBr and NaClO are generally used as catalysts and primary oxidants in the pH range of 9−11. The cellulose content of the starting material often dictates the specifics of the TEMPO oxidation process. For example, when relatively pure cellulosic materials or bleached lignocellulosic materials are used, TEMPO oxidation can be applied directly.[60] When the starting material has a significant lignin composition, however, a delignification step is typically required prior to TEMPO oxidation.[22,26,31] Baati et al. performed a TEMPO oxidation with NaBr and NaClO at pH 10 on bleached wood cellulose fiber (pretreated via $NaClO_2$/acetic acid delignification) prior to fibrillation with TSE.[22] It was found that a higher carboxyl content (900 μmol/g) resulted in a higher yield of nanofibrillated material and significantly reduced the fibers suspension gelation time during the extrusion process. Similar results with regard to the effect of the carboxyl content on the yield and viscosity of CNFs were observed by Boufi et al. during fibrillation employing a high speed blender.[26]

A range of other chemical treatment methods have been successfully applied in nonconventional fibrillation processing. Specifically, surface modifications, such as carboxymethylation, phosphorylation, and sulfethylation, have been shown to introduce surface charges on cellulose fibers and to decrease energy consumption during fibrillation.[19,23,61] For example, Rol et al. applied phosphorylation to bleached *Eucalyptus* kraft pulp using urea and ammonium phosphate dibasic solution and found that phosphorylation reduced the energy consumption required for CNF production via TSE.[19] It is noted that acid catalysts have also been successfully used as pretreatments of cellulosic feedstocks prior to mechanical fibrillation at proper conditions.[62]

Green solvents, particularly ionic liquids (ILs) and deep eutectic solvents (DESs), have recently been utilized as pretreatment in CNF production.[52,53] ILs and DESs have unique properties, including extremely low vapor pressure, high thermal and chemical stability, low-flammability, etc.[63−65] More importantly, these solvents can dissolve biomass[66−68] and have catalytic activity,[69,70] properties that make them highly attractive for biomass pretreatment. It is noted the DESs are more cost-effective and easier to synthesize than ILs. The application of DESs in nonconventional fibrillation is an emerging field. For example, Ninomiya et al.[52] applied a choline acetate/dimethyl sulfoxide (ChoAc/DMSO) DES system to pretreat bagasse at 100 °C before fibrillation with a high speed blender. The CNFs obtained from the ChoAc-treated bagasse had five times greater surface area than CNFs that had not undergone the pretreatment. Importantly, the crystallinity of the fiber remained the same as that of the starting materials. Separately, Taheri et al.[71] employed a potassium carbonate/glycerol DES system to pretreat wood sawdust at 100 °C for 18 h before fibrillation using TSE. It was

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

Table 1. Characteristics of CNFs Produced by Nonconventional Fibrillation Methods

	fibrillation methods	feed stocks	pretreatment/post-treatment	diameter (nm)	degree of fibrillation	D.P.[l]	crystal index (%)	light transmittance (%)	ref
extrusion	extrusion with wet pulp (40 min)	*Eucalyptus Grandis* wood pulp (10 wt %)	TEMPO[c] oxidation (500 μmol/g)	3−7	81%[Y.F.,g] 724[WRV,h]	N.A.	N.A.	suspension, 75% (λ = 600 nm)	22
	extrusion with wet pulp (20 min)	never-dried *Eucalyptus* pulp (10 wt %)	TEMPO oxidation (base) (1000 μmol/g)	3−9	64% [Y.F.] 454[WRV]	N.A.	77	suspension, 61%, (λ = 600 nm)	44
	extrusion with wet pulp (20 min)	never-dried *Eucalyptus* pulp (10 wt %)	carboxy-methylation (820 μmol/g)	N.A.	58% [Y.F.] 486 [WRV]	N.A.	57	suspension, 57% (λ = 600 nm)	44
	extrusion with wet pulp (10 passes)	refined needle-leaf bleached kraft pulp (28 wt %)	8-pass Refined	∼50	780 s[D.T.,i]	900	76	N.A.	77
	extrusion with wet pulp (7 passes)	disk-beater refined *Eucalyptus* bleached kraft pulp (∼20 wt %)	TEMPO oxidation (820 μmol/g)	34.6	37%[Y.F.]	260	65	N.A.	18
	extrusion with wet pulp (7 passes)	disk-beater refined *Eucalyptus* bleached kraft pulp (∼20 wt %)	enzyme (300 ECU[e]/g)	25.8	65%[Y.F.]	200	72	N.A.	18
	extrusion with wet pulp (7 passes)	disk-refined Eucalyptus bleached kraft pulp (17 wt %)	enzyme (300 ECU/g)	52	64.3%[Y.F.]	218	N.A.	289[T.n]	23
	extrusion with wet pulp (7 passes)	disk-refined *Eucalyptus* bleached kraft pulp (17 wt %)	cationized (DS[d] = 0.31)	43	54.6%[Y.F.]	731	N.A.	113[T.]	23
	extrusion with wet pulp (4 passes)	disk-refined *Eucalyptus* bleached kraft pulp (10−20 wt %)	enzyme (300 ECU/g)	40	51.2%[F.C.,j] 74.2%[Y.F.]	260	N.A.	384[T.]	19
	extrusion with wet pulp (4 passes)	disk-refined *Eucalyptus* bleached kraft pulp (10−20 wt %)	phosphorylated (DS = 0.1−0.2)	40	8.6[F.C.] 33.8%[Y.F.]	580	N.A.	214[T.]	19
	extrusion with wet pulp modified screw (1 pass)	disk-refined *Eucalyptus* bleached kraft pulp (20 wt %)	enzyme (300 ECU/g)	20.2	49.1%[F.C.] 69.4%[Y.F.]	270	N.A.	397[T.]	24
	reactive extrusion NaOH (1×), H_2SO_4 (2×)	milled soybean hull (32 wt %)	N.A. /ultrasonication post-treatment	80−100	50%[k]	N.A.	62	N.A.	32
	reactive extrusion H_2SO_4 (1×)	bleached milled soybean hull (32 wt %)	N.A. /ultrasonication post-treatment	80−100	60%[k]	N.A.	73	N.A.	32
	reactive extrusion NaOH (1×), H_2SO_4 (2×)	milled oat hull (32 wt %)	N.A. /ultrasonication post-treatment	100	60%[k]	N.A.	68	N.A.	78
	reactive extrusion H_2SO_4 (1×)	bleached milled oat hull (32 wt %)	N.A. /ultrasonication post-treatment	80−100	65%[k]	N.A.	80	N.A.	78
ball milling	PFI mill (30 000 revolutions)	bleached birch kraft pulp	periodate oxidized	10−100	N.A.	N.A.	65	film, ∼30% (λ = 550 nm)	49
	planetary mill (400 rpm, 2 h)	cellulose powder	none	10−25	93.1%[Y.F.]	N.A.	65.8	N.A.	53
	tumbler mill	dry bleached softwood kraft pulp	mechanical blending, alkaline	139−793	N.A.	N.A.	>70	N.A.	79
		wheat straw, Kenaf fibers	acids, peroxide, alcohol, alkaline	8−100	N.A.	N.A.	∼70	N.A.	80
	attritor mill (0.5−3 h, 1000 or 3000 rpm)	grass (*Triodia pungen*)	bleaching and delignification	8.7 ± 4.8	N.A.	N.A.	∼70	N.A.	81
blending	blender (45 000 rpm, 5−60 min)	bagasse (dewax, delignified, and alkali washed)	acetylation	50	N.A.	N.A.	63−73	film, ∼75% (λ = 500 nm)	82
	blender (5000, 10000, or 37000 rpm, 1−60 min)	Japanese cedar pulp	bleaching	15	N.A.	N.A.	69−71	resin infused CNF film, 70% (λ = 550 nm)	83
	blender (11 000 rpm, 15−20 min)	triticale straws	delignification, bleaching, TEMPO	20	∼90%[Y.F.]	N.A.	74	suspension, 85%	27
	blender (11 000 rpm 15−30 min)	corn stalk	delignification, bleaching, TEMPO	3−5	∼90%[Y.F.]	N.A.	N.A.	suspension, 85% (λ = 600 nm)	26

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

Table 1. continued

	fibrillation methods	feed stocks	pretreatment/post-treatment	diameter (nm)	degree of fibrillation	D.P.[l]	crystal index (%)	light transmittance (%)	ref
steam explosion	3 stages: 1.4 bar, 110−120 °C, 1 h^{first}, 3 h, 15 min^{third}	banana fiber	alkaline and bleaching/stir	10 μm	N.A.	N.A.	N.A.	N.A.	33
	9 stages: 1.4 bar, 1 h^{first}, 15 $min^{second\text{-}ninth}$	banana fiber	alkaline and bleaching/stir	<40	N.A.	N.A.	74	N.A.	84
		pineapple leaf fibers	alkaline and bleaching/stir	5−60	N.A.	N.A.	74	N.A.	85
	1.5 bar, 121 °C, 1 h	oil palm empty fruit bunch fibers	alkaline/ultrasonication	50	N.A.	N.A.	N.A.	N.A.	86
aqueous counter collision	180 cycles	MCC[a]	none	14	N.A.	210	50	N.A.	87
	60 cycles	BC[b]	homogenization	34	55.9 $^{SSA,\ FD,(l)}$/ $m^2 \cdot g^{-1}$	240	70	N.A.	88
	30 cycle, 160 μm (D), 180 MPa, 170°	rice straw	delignification and hemicellulose removal	<200	$100\%^{Y.F.}$	N.A.	79	suspension, 20% film, ∼20% (λ = 500 nm)	28
	30 cycles, 140 μm (D), 200 MPa, 170°	bleached kraft pulp	beater refining/ ultrasonication	25	$80-85\%^{Y.F.}$	N.A.	∼60	N.A.	73
ultrasonication	30 min, 20−25 kHz, 1 kW	wood, bamboo, wheat straw, flax fibers	delignification, hemicellulose removal	10−40	N.A.	N.A.	60−80	N.A.	89
	30 min, 20 kHz, 1.2 kW	MCC	water soaking	∼100	239^{WRV}	N.A.	N.A.	N.A.	90
	20 min, 20−25 kHz, 1.2 kW	bleached hard kraft pulp	alkaline	50−150	N.A.	626	60	CNF/PVA film, 70% (λ = 550 nm)	91
	10 min, 20 kHz, 0.75 kW	bagasse fibers	delignification, refining, enzyme	∼30	N.A.	N.A.	∼70	N.A.	58
	20 min, 150 W	hardwood kraft pulp	enzymes (1 mg/g for each)	∼140 nm	470^{WRV}	∼550	71	suspension, 37%, (λ = 600 nm)	76
	1 h 50 min, 0.75 kW	cellulose fibers	hydrodynamic cavitation	301 nm	N.A.	N.A.	38	N.A.	92
cryocrushing	N.A.	bleached softwood pulp	disintegrating	<1 μm	$89\%^{Y.F.}$	N.A.	N.A.	N.A.	5
	N.A.	bast fiber, rutabaga	alkaline, acid	40	N.A.	N.A.	54	N.A.	93
other methods	pH-induced self-fibrillation	bleached softwood kraft pulp	oxidation (TEMPO, periodate)	∼20	$95\%^{Y.F.}$	N.A.	75	film, 90% (λ = 600 nm)	94
	microwave hydrothermal	pea waste	TSE[f]	5	$40\%^{Y.F.}$	N.A.	∼30	N.A.	43

[a]Microcrystalline cellulose. [b]Bacterial cellulose. [c]2,2,6,6-Tetramethylpiperidine-1-oxyl. [d]Degree of substitution. [e]Endo cellulase units. [f]Twin-screw extrusion. [g]Yield of fibrillation. [h]Water retention value. [i]Dewatering time. [j]Fines content. [k]Measured dry weight. [l]Specific surface area from freeze-drying. [m]Degree of polymerization. [n]Turbidity. [o]Poly(vinyl alcohol).

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Biomacromolecules 2021, 22, 4037−4059

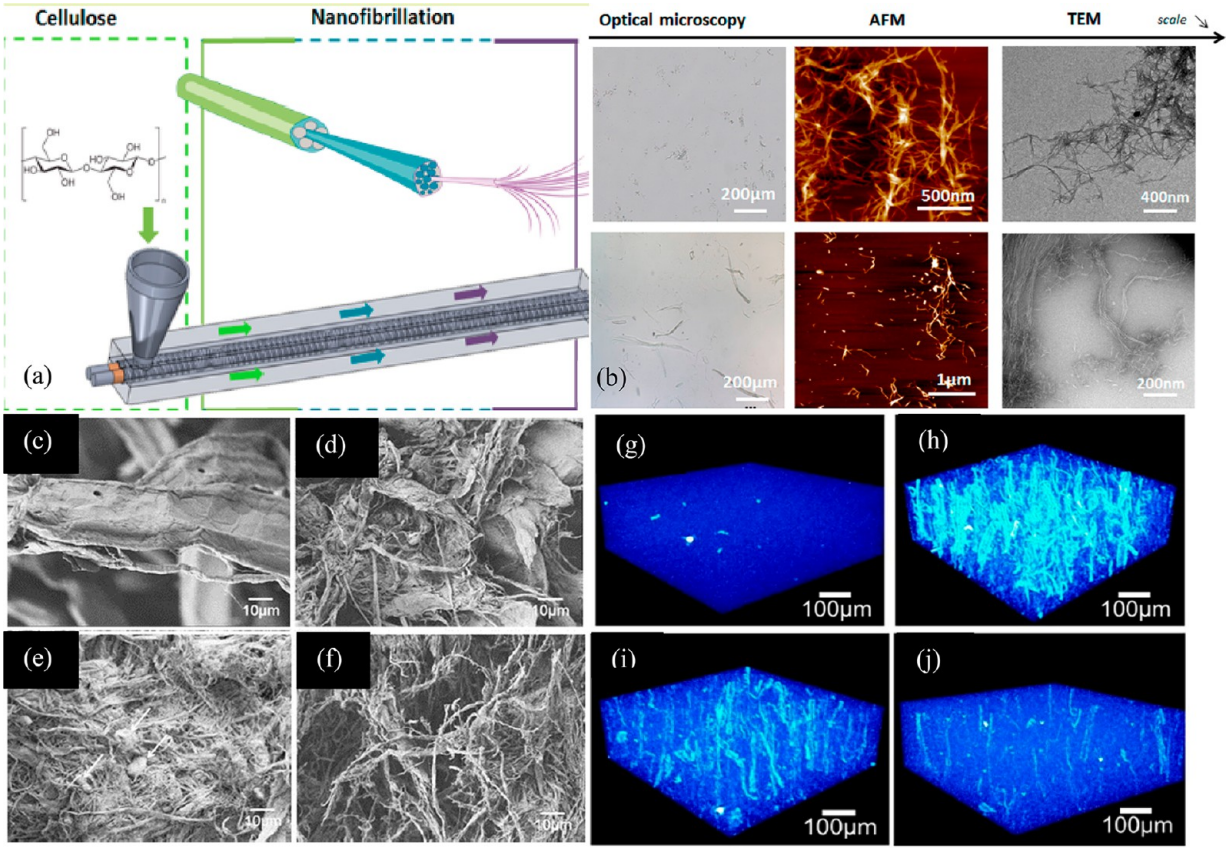

Figure 2. Schematic drawing of extrusion fibrillation of pulp fibers (a) and microscopic images of resulting CNFs (TEMPO-mediated oxidation and 7 passes of extrusion) (b). Reprinted from ref 18 with permission. Copyright 2017 American Chemical Society. SEM micrographs of materials used at different stages of extrusion fibrillating pulp fibers with polymers: never-dried kraft pulp (NDKP) (c), refiner-treated NDKP (d), a mixture of NDKP, powdered polypropylene (PP), and maleic anhydride-grafted PP (MAPP) after extrusion fibrillation (e), and CNFs after matrix removal by *p*-xylene washing (f). Scale bar: 10 μm. Reprinted by permission from Springer Nature ref 96. Copyright 2013. X-ray computed tomography images of injection-molded samples of pure high-density polyethylene (HDPE) (g), HDPE (77 wt %)/pulp fiber (10 wt %) composite with a degree of substitution of 0 (h), 0.22 (i), and 0.43 (j) from the one-step, dry-pulp direct kneading method. Reprinted from ref 97. Copyright 2018 with permission from Elsevier.

found the DES treatment improved the degree of the fibrillation and resulted in less fiber breakage. In another study, Yu et al.[51] employed a choline chloride-oxalic acid dihydrate DES to pretreat Ramie fiber, followed by ball-milling. The CNF produced had a very high cellulose content, up to 90%, and the DES pretreatment reduced the required milling time from 12 h for a standard bleached feedstock to 6 h.

3.2. Mechanical Pretreatments. Mechanical pretreatment of lignocellulosic feedstocks has been used for prefibrillation or size reduction in order to reduce energy expenditure during fibrillation processes. Mechanical size reduction has also been shown to reduce clogging issues during fibrillation. Various mechanical processes including disk refining and milling have been employed as pretreatments. Disk refining (DR) has been extensively used for the fibrillation of CNFs and is commonly combined with chemical or enzymatic pretreatments.[1,47] However, DR has also used as a mechanical pretreatment prior to fibrillation via other processes. For example, Rol et al.[18,19,23,72] has investigated DR pretreatment prior to the TSE fibrillation process and shown that the refining pretreatment process only consumed 0.68 kWh/kg and reduced the overall fibrillation energy by 13%. Milling is an alternate and an effective means of decreasing the size of lignocellulosic materials. Tsalagkas et al.[73] applied dry-state ball milling (BM), and separately a Valley beater (VB), to pretreat bleached softwood and hardwood fibers for fibrillation using an aqueous counter collision (ACC) system. The BM-treated feedstocks had lower yields and crystallinity index (CI) than the VB-treated feedstocks. The lower CI for the BM feedstocks was potentially caused by the rupture of crystalline regions of cellulose during processing. However, energy expenditures of the milling processes were not reported, nor was their contribution to the overall energy consumption required for fibrillation.

3.3. Biochemical Pretreatments. Biological pretreatment, especially enzyme pretreatment, has been reported to reduce the energy required to fibrillate biomass to CNFs.[74] Appropriate enzymes act to hydrolyze cellulose and thereby facilitate mechanical fibrillation. Typically, *cellobiohydrolase* and *endoglucanase* enzymes are employed for feedstock pretreatment, which targeting the crystalline and amorphous regions of cellulose, respectively. Prior to enzymatic treatment, biomass feedstocks are often delignified and/or bleached to increase the accessibility of the enzymes to cellulose. Rol et al.[19,23,75] pretreated bleached *Eucalyptus* kraft pulp with an *endoglucanase* enzyme, followed by fibrillation with TSE. The CNFs produced from the enzyme-treated fibers had a lower degree of polymerization (DP) compared to nontreated fibers;[75] however, the energy consumption was much lower. Additionally, the turbidity of the enzyme-pretreated CNF slurry was

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significantly higher than that of the nonpretreated analog. An enzymatic complex (*endoglucanase, lytic polysaccharide monooxygenase (LPMO), and xylanase*) was applied to hardwood kraft pulp to evaluate their efficiency in facilitating fibrillation via sonication.[76] Such a complex system positively enhanced the accessibility, degree of polymerization, crystallinity, and surface charge of pulp fiber, resulting in a more uniform CNF morphology.

It has been shown that the efficacy of enzymatic pretreatment is heavily dependent upon the accessibility of cellulose. Indeed, the higher the surface area of the biomass feedstock, the greater the energy reduction required for defibrillation after the enzyme treatment. A combination of mechanical and chemical/enzymatic pretreatments can be more effective for reducing the energy of fibrillation. For instance, Rol et al.[18] studied the effect of different pretreatment strategies on the energy required for fibrillation employing TSE with *Eucalyptus* bleached kraft pulp. Enzymatic hydrolysis and TEMPO oxidation were performed on disk-refined pulp fibers and benchmarked with the energy requirement of fibrillation process using a grinder. With the disk-refining step, the energy required for TSE fibrillation was reduced for both enzymatic (from 20 to 6 kWh/kg) and TEMPO-oxidized (from 20 to 12 kWh/kg) pulp fibers. The disk refining pretreatment only consumed about 0.68 kWh/kg of energy.

4. NONCONVENTIONAL FIBRILLATION METHODS

This section focuses on how CNFs were previously prepared by various nonconventional fibrillation methods. To facilitate the comparison among research, most important factors (processing parameter, feedstock type and pre/post-treatment) that can change the degree of fibrillation of CNFs are summaried in Table 1. Also listed are mechanical and physical properties of resulting CNF products. A few examples are discussed in details to highlight their importance.

4.1. Extrusion. Extrusion processes are widely used in various industrial sectors for manufacturing. Heiskanen et al. demonstrated approximately a decade ago that extrusion could also be used to produce CNFs from woody biomass.[95] A summary of the extrusion work that has been performed and the resulting properties of the CNFs are presented in Table 1. It is evident from Table 1 that two common types of extrusion fibrillation have been studied. The first method comprises direct extrusion of never-dried pulp fibers or fibers dispersed in solvents (mostly water) using TSE.[22] The second method is similar to the first, with the addition of chemical reagents to a wet feedstock immediately prior to extrusion with sing-screw extrusion (SSE). There is a third extrusion method which involves the extrusion of wet cellulose fibers together with a polymer in the solid state.[96] In all cases, the shear forces produced during extrusion have been reported to fibrillate the cellulose fibers into micron or nanoscale fibers, or a combination of both. There are several advantages in using extrusion to fibrillate cellulose fibers as compared to using conventional fibrillation methods. First, extrusion is a continuous process with a reasonable production rate (1.2 kg/h of dry materials).[18] Second, CNF suspensions with very high solids contents (up to 40 wt %) can be achieved using extrusion versus the few weight percent typically employed.[77] The high solids contents of CNF slurry greatly reduces their transportation cost. Third, the extruder screw configuration can be readily altered to modify the degree of fibrillation, thereby lowering the initial R&D time and cost.[18] Fourth, the reported energy consumption of extrusion (2−6 kWh/kg[18,19,22−24]) is potentially lower than that of conventional fibrillation methods (e.g., 20 kWh/kg for homogenizing[17]). Fifth, extrusion processes generally do not experience fiber clogging as conventional methods do.

4.1.1. Extrusion with Wet Pulp. A schematic representation of cellulose fiber fibrillation employing TSE is presented in Figure 2a. Wet cellulose fibers are introduced directly into TSE. Cellulose fibers in the region between the screws and the inner wall of the surrounding barrel experience high shear forces and are defibrillated into smaller fibers. Cellulose fibers are often passed through the extruder several times in order to achieve sufficient fibrillation when employing a conventional screw profile. It is noted however that overprocessing can cause severe degradation in the degree of polymerization of CNFs.[77] Factors affecting the fibrillation of cellulose include screw design (amount of shear forces), pre- and post-treatment, the feedstock employed etc.

Ho et al. published one of the earliest reports of CNF production via extrusion employing never-dried kraft pulp (NDKP) with TSE at solids contents of up to 45 wt %.[77] Notably, during extrusion, the temperature inside the barrel rose to greater than 70 °C due to friction, resulting in a loss of water via evaporation. As such, circulating coolants were employed to maintain the process temperature at values less than 40 °C and thereby prevent water evaporation and concomitant discoloration of fibers. It was found that increasing the number of extrusion passes improved the degree of fibrillation, however, the degree of polymerization was reduced, the crystallinity was negatively impacted, the mechanical properties decreased and the thermal stability worsened. The particle size distribution of the CNFs produced was relatively broad, with a population of large particles exceeding 100 nm in diameter. Rol et al. furthered the study of TSE fibrillation of pulp fiber via examination of the effect of pretreatments employing TEMPO oxidation and enzymatic hydrolysis.[18] Micrographs of the resulting CNFs are presented in Figure 2(b). The authors pointed out that the overall morphology of CNFs from extrusion fibrillation was similar to those from grinding. TEMPO-oxidized pulp fibers did not undergo extensive fibrillation, with only 37% of the sample being on the nanoscale after 7 extrusion passes. Enzyme-pretreated pulp fibers however had a much greater nanoscale fraction (∼70%) after 7 passes through a TSE, with a similar morphology to CNFs created via a super mass colloider.[18] It is noted that the combination of pretreatments and TSE did not significantly impact the crystallinity of the fibers. However, the degree of polymerization was less than that of CNFs created via solely TSE. It is well-known that fibrillating enzyme-pretreated pulp fibers can save considerable energy during CNF production. Employing a comparable approach, cationized- or phosphorylated-CNFs were produced by TSE.[23] The cationized-CNFs had comparable fiber properties to those produced employing enzymatic pretreatments. The phosphorylated samples consisted of large micron-scale fiber fractions with a smaller amount of nanofibers.[19] To improve the fibrillation efficiency of TSE, Rol et al. recently simulated and verified a modified screw profile to produce CNFs with a single pass TSE.[24] The optimized screw profile comprises 6 kneading zones that exert high shear on the fibers. The CNFs produced from a single pass through the optimized screw profile exhibited similar properties to those made from 4 passes

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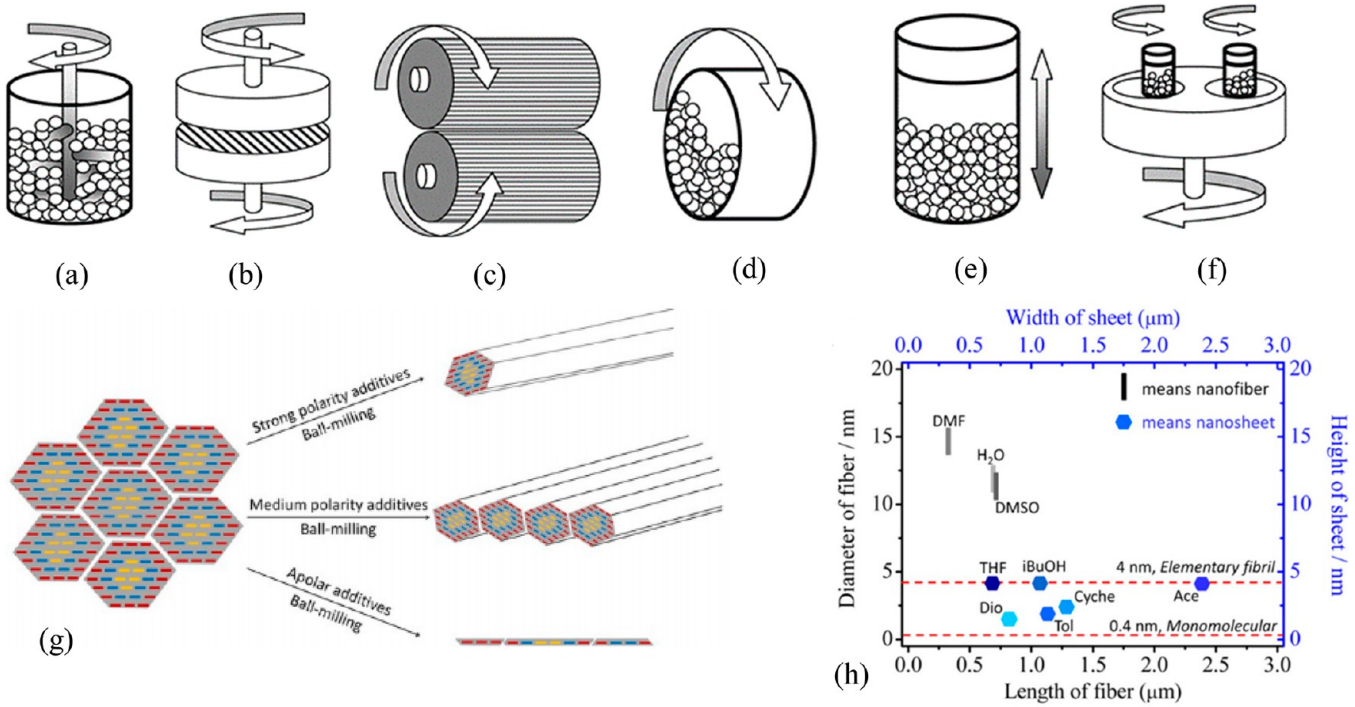

Figure 3. Schematic drawing of direct and indirect balling processes: (a) attritor mill, (b) pan mill, (c) roll mill, (d) tumbler ball mill, (e) vibratory (or shaker) mill, (f) planetary ball mill. Republished with permission of Royal Society of Chemistry, from ref 105; permission conveyed through Copyright Clearance Center, Inc. Scheme of cellulose ball-milled in the different solvents with strong polar, medium polar and apolar conditions (g). Statistical size distributions of CNFs obtained by ball-milling with varying solvent polarities (h). Reprinted from ref 108 with permission. Copyright 2020 American Chemical Society.

through a classic TSE, without an increase in the total energy consumption.

Employing a laboratory-scale mini TSE with no kneading elements other than a common conical, intermeshing and corotating configuration, Baati et al. produced CNFs from TEMPO-treated pulp fibers.[22] In the absence of high-shear kneading elements, the temperature of the material was maintained at approximately 30 °C during extrusion, despite continuous processing for a period of 40 min. Employing a feedstock generated via a $NaClO_2$/acetic acid pulping process, a carboxyl content of 300 μmol/g on cellulose fibers was reported to be sufficient to facilitate nanofibrillation. The authors found that no significant fibrillation could be achieved when employing traditional NaOH-treated pulp fibers even after an oxidative pretreatment, a finding potentially attributable to the limited shearing capacity of the mini-TSE. To fibrillate commercially produced never-dried pulp, the authors explored more extensive TEMPO oxidation and carboxymethylation pretreatments.[44] The pH level of TEMPO oxidation was deliberately raised to 10 to achieve a carboxyl content as high as 1350 μmol/g. By fibrillating pulp fibers modified with either TEMPO oxidation or carboxymethylation at a carboxyl content of 800 μmol/g, a 50 wt % fraction of nanoscale material was achieved. Further elevating the carboxyl content of pulp via alkline TEMPO oxidation to 1350 μmol/g yielded a nanoscale fraction as high as 92 wt %.

4.1.2. Reactive Extrusion. Reactive extrusion has been investigated to fibrillate soybean hulls (SH) into CNFs with diluted chemical solutions.[32,78] Using SSE with heating (110 °C), SH can be nanofibrillated when proper treatments and parameters were applied. For unbleached SH, 1 pass SSE in the presence of NaOH (10 wt %), followed by 2 passes with H_2SO_4 (2 wt %) and finally an ultrasonication post-treatment, successfully generated CNFs.[32] The NaOH and H_2SO_4 solutions were employed to partially remove hemicellulose and lignin from the SH, which facilitated fibrillation. Alternatively, bleaching SH with peracetic acid, followed by a single pass SSE in the presence of H_2SO_4 and an ultrasonication post-treatment, also resulted in the production of CNFs. It is noted that a comparable approach applied to oat hulls achieved similar fibrillation results.[78] The authors state that their reactive extrusion methods are more effective and environmentally benign than traditional fibrillation techniques as the processing time is shorter, the concentrations of the chemical reagents employed are lower, and the reagents themselves are less harmful than those employed for traditional techniques.

4.1.3. Coextrusion with Polymers. Rather than extruding a biobased feedstock alone, or in the presence of a solution, the feedstock can be extruded in the presence of a grinding medium. Most commonly, the grinding medium employed has been powdered polymers, with the resultant product being a micro/nanofibrillated cellulose network with entrained polymer.[97,98] Such a mixture forms a structure that is highly beneficial for fiber dispersion when compounding followed by either wet or dry extrusion. Little work has been performed to characterize the CNFs generated via the coextrusion process since to do so would require separating the CNFs and their embedded polymer particles. Indeed the only study to investigate CNFs separated from the polymer residue created by coextrusion was that conducted by Taheri et al., in which CNFs were separated from hydroxyethyl cellulose (HEC) via vacuum filtration after extrusion fibrillation.[98]

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The majority of the work centered on coextrusion of biomass with polymers has been conducted by researchers at Kyoto University.[96,97,99−101] Initial work focused on a two-step process (in situ fibrillation followed by wet extrusion-compounding). However recently a one-step, dry-pulp direct kneading method has been reported.[97] Representative images of the CNFs generated from the two-step process are presented in Figure 2 (f). Specifically, NDKP (10−50 wt %) was first mixed with a polyolefin and a coupling agent via an agitator. The mixture was then kneaded in an extruder at 0 °C and 400 rpm. The same extruder was subsequently employed for wet compounding of the resultant mixture at 180 °C and 200 rpm, followed by pelletizing and injection molding. Two methods were used to qualitatively characterize the resultant fiber morphology: SEM on CNFs before and after matrix removal, and direct X-ray computed-tomography (CT) scans on CNF/polymer composites. As can be seen in Figure 2c−f, the fiber diameters ranged from a few to several tens of microns.[96] To improve the efficiency of *in-situ* fibrillation and compounding, the feedstock was changed from NDKP to acetylated pulp fibers.[97] Recently, a mixture of dried acetylated pulp fibers, polyolefin powders and coupling agent powders was fed directly into an extruder to be melt compounded before pelletizing and injection molding.[97] On the basis of the X-ray CT graphs presented in Figure 2g−j, the one-step approach unambiguously showed an improved fiber dispersion as compared to the two-step method. However, attention should be paid to the difference in fiber contents in the composites.[97,101]

Hietala et al. attempted to fibrillate pulp fibers in the presence of thermoplastic starch (TPS) by melt extruding a wet mixture of (treated) pulp fiber, TPS, and processing aids.[102] Even with a high degree of carboxyl content (1300 μmol/g) after TEMPO-mediated oxidation, pulp fibers were not largely fibrillated into nanofibers. One potential explanation for the lack of fibrillation is that excessive water (70 wt %) in the mixture reduced the viscosity of the melt during extrusion, thereby lowering the shear forces experienced by the fibers. Indeed, Cobut et al. melt extruded a mixture of TEMPO-treated (980 μmol/g) pulp fiber, TPS and processing aids, at a much lower water content (17 wt %).[103] Some nanofibrils with 30 nm in diameter were observed along with a population of microfibrils. Fourati et al. extrusion fibrillated a mixture of TEMPO-oxidized (740 μmol/g) pulp fiber, TPS, and processing aids at an intermediate water content (42 wt %) and low extrusion temperature (25 °C), before increasing the extruder temperature to melt compound the mixture.[104] The authors reported that the pulp fibers were mostly disintegrated into micro and nanoscale fibers. Finally, Taheri et al. fibrillated never-dried softwood pulp with hydroxyethyl cellulose into CMFs using TSE with a single pass.[98] It was found that reducing the amount of polymer in the mixture (50−20 wt %) shifted the peak of the particle size distribution to smaller values (13.65−12.22 μm) and decreased the aspect ratio (47−32) of the fibrillated fibers. The authors believed that HEC acted as a lubricant and reduced the fiber breakage during extrusion.

4.2. Ball-Milling. CNFs have been produced via ball-milling of cellulosic feedstocks for many years. Ball milling may be characterized as either direct or indirect (Figure 3).[105] Direct milling utilizes contact between the milling surface (e.g., rotating gears or shearing blades) and the material being processed to reduce particle size. There are three major forms of direct milling: attritor mill, pan mill, and roll mill (Figure 3a−c).[106] Indirect milling utilizes an additional medium as the milling surface, often in the form of weighted balls. There are three major forms of indirect milling: tumbler ball mill, vibratory (or shaker) mill, and planetary ball mill (Figure 3d−f).[106] Indirect milling transfers mechanical energy generated by the mill to the material being processed and does so in the following order: planetary > vibrational > tumbling mill.[72,107] A large portion of the energy generated (~80%) is lost as dissipated heat.[105] Heat loss can be mitigated to some extent by adjusting process conditions. For example, an increase in solids content during fibrillation can limit the amount of heat dissipated into the solvent. Processing conditions can also significantly impact the physical properties of the resultant material. For example, Liimatainen et al. determined that an increase in solids content from 7.5 to 15 wt % resulted in an increase in tensile strength and elongation of the resulting CNF films, from 61.1 to 113.1 MPa and 6.8% to 15.9%, respectively.[49] The better heat dissipation in this higher solid content sample produced a mechanically robust, interpenetrating CNF matrix.

Researchers have worked to optimize ball-milling conditions for CNF production by studying the effects of various parameters on CNF properties. For example, Zhang et al.[108] and Ago et al.[109] studied the effect of solvent additives and their polarity on fibrillation efficiency (Figure 3g and h). Use of polar solvents enabled the production of long, thin CNF fibers, potentially attributable to the solvents ability to penetrate the cellulose fibers. Conversely, use of solvents with reduced polarity resulted in sheet-like material, potentially attributable to the solvents inability to penetrate the cellulose fibers. Additionally, to minimize hydrogen bonding and other intermolecular interactions present in cellulose, researchers have developed additives to weaken these bonds and assist fibrillation. Some of these additives induced simultaneous fibrillation and surface functionalization during the ball-milling process.[110,111] Finally, many studies have demonstrated that longer ball-milling times result in CNFs with lower aspect ratios.[56,72,112] Increased ball-milling time results in a longer interaction between the media and milled material, which produces greater damage and separation of the cellulose, leading to poor physical properties. Indeed, Zeng et al. determined that the degree of polymerization of CNFs decreased from approximately 350 to 200 when the ball milling processing time increased from 30 min to 3 h.[56]

4.3. Blending. CNF fibrillation methods have been developed using high shear blending techniques, many of which utilize household equipment to produce CNFs at a final solid content lower than 2 wt %.[26,31,82,83,113] It is noted however that in many cases, optimization of the operating conditions is challenging as minimal variations in process parameters would produce CNFs with significantly different qualities. Specifically, changes in blender speed, blending time, and solids content have been shown to affect the CNF morphology and other properties. For example, Sofla et al. observed that an increase in blending time from 5 to 30 min resulted in a decrease in CNF diameter from approximately 135 to 40 nm.[82] Uetani et al. observed similar results and demonstrated via optical imaging that ballooning of fibers and uncurling of fiber ribbons occurred.[83] Not surprisingly, the longer blending times resulted in a decrease in crystallinity from 72% to 69%. Overall, this fibrillation method is promising as it produces CNFs with a range of properties and does not

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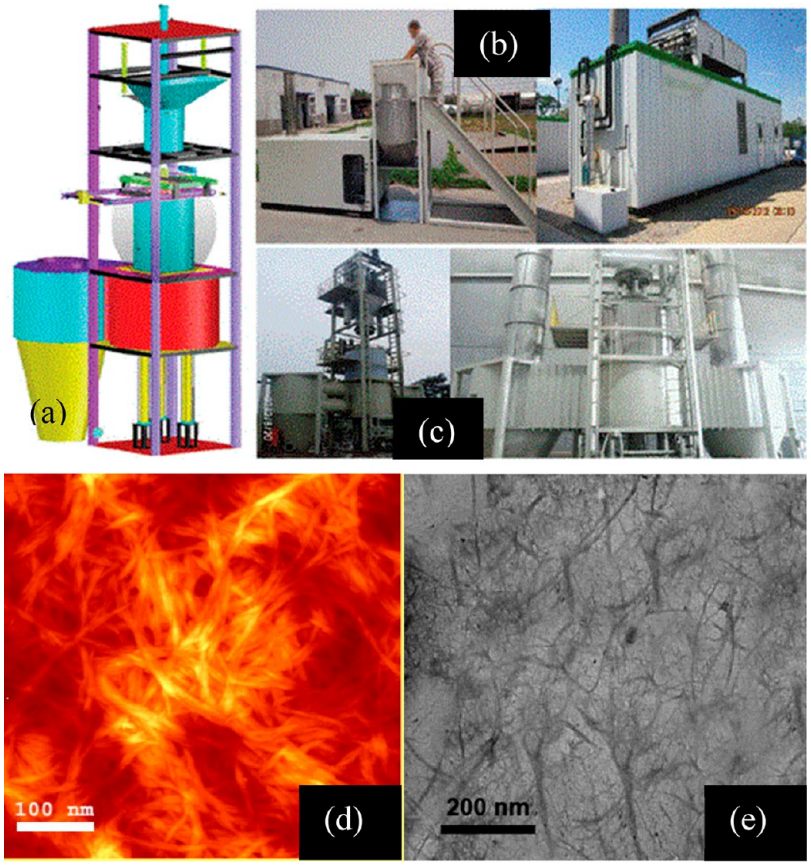

Figure 4. Diagram of a steam explosion device consisting of piston/cylinder to generate high pressures for defibrillation (a), steam explosion equipment of 100 L chamber (b), and an industrial-scale chamber of 10 m^3 (c). Reprinted from ref 115 with permission. Copyright 2018 American Chemical Society. Images of steam-explosion generated CNFs with AFM (d) and TEM (e). Reprinted from ref 85. Copyright 2010 with permission from Elsevier.

require the use of expensive, specialized equipment. However, work is required to optimize the blending parameters to produce predictable and tailorable CNFs.

4.4. Steam Explosion. A novel method for production of CNFs is the utilization of steam explosion as a thermomechanical defibrillation method. Steam explosion was first employed as a biomass treatment method in 1927 by Mason for defibrillating wood into fibers for hardboard production.[33,84,114] The advantages of steam explosion as a biomass treatment method include a low environmental impact, relatively low energy consumption, low capital investment, and less hazardous process chemicals are used.[114] Fiber products from steam explosion have interesting applications. For example, Yan et al. used steam explosion to convert lignocellulosic biomass to dietary fiber.[115] Additionally, Cherian et al. steam exploded pineapple leaf fibers to produce CNFs with utility in biomedical applications, including issue engineering, drug delivery, wound dressings, and medical implants.[85]

For CNF production, dry lignocellulosic biomass materials are loaded into a pressure device such as an autoclave or a custom cylinder/piston device (Figure 4).[115] An alkaline pretreatment may be employed to increase surface roughness of the biomass material to enhance water penetration, and to remove noncellulosic components.[116] The pressure vessel is subsequently charged with water and pressurized to 10−35 bar at temperatures in the range of 180−240 °C (reaction conditions are selected based on desired crystallinity and degree of polymerization of the product). The pressure is subsequently dropped to ambient, resulting in a steam explosion and fibrillation of the biomass. Multiple cycles of steam explosion are typically implemented to limit the amount of exposure of the cellulose to the harsh conditions that would be required if a single cycle was performed. Higher temperatures and pressures result in greater degradation of the cellulose and lowered crystallinity and degree of polymerization. In one study, lowered steam explosion conditions of 2 bar and 120 °C were utilized to generate CMFs.[116]

The key to success of steam explosion as a novel CNF production method is its ability to separate the lignocellulosic material into its three main constituents: cellulose, hemicellulose, and lignin. With cellulose being the desirable material, it is important that hemicellulose and lignin can be removed easily during or after the process. The steam explosion process, along with chemicals, results in the hydrolysis of hemicellulose and the depolymerization of lignin.[33,84−86,114−118] Once the relevant bonds are broken, the components may be separated. The hemicellulose fraction can be dissolved in water, while the depolymerized lignin can be dissolved in an alkaline solution or an organic solvent. After steam explosion treatments, the structural, morphological, and thermal characteristics of the cellulose nanofibers are typically examined. Specific steam explosion process parameters employed in the production of CNFs, and the resultant CNF properties are listed in Table 1. Though steam explosion has long been used to extract cellulose fibers from biomass, the

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efficacy and quality of CNFs produced remain problematic.[1] Therefore, in some studies, steam explosion has been applied as a pretreatment for subsequent fibrillation of CNFs by homogenization[114−116,118] and grinding.[117]

4.5. Aqueous Counter Collision (ACC). CNFs can be prepared by disintegrating cellulose fibers with an aqueous counter collision (ACC) system, which typically consists of an inlet reservoir, an intensifier pump unit, an interaction chamber, and a connecting conduit, as well as check valves, gauges, cooling coils and heat exchangers. First, cellulose fibers are dispersed in water, and the resulting suspension is stored in a reservoir. The pump aspirates a portion of the suspension, pressurizes and injects the slurry up to 245 MPa, and forces it to travel through the system at a speed up to 500 m/s.[87] An ACC system divides the pressurized suspension into two channels that form a pair of water jets which collide into each other in the interaction chamber. The streams collide at an adjustable oblique angle up to 180°, as shown in the Sugino Machine's Star Burst System (Figure 5a). Impact forces originate from collisions with the microchannel walls and with the fluid itself. A change in velocity or direction exposes the entrained particles to a high shear field and occasional cavitation. The sample, exiting via the heat exchanger or cooling coil outlet, is collected and recirculated or poured back into the reservoir to enable multiple passes, if desired. The advantages of ACC method include nearly 100% yield and capable of producing fibrils from a wide range of polymeric materials with hierarchical structures.[87] ACC systems have also been designed with continuous processing capabilities. Ideally, they should be designed to output particles below a certain size while continuing to mill particles above that size, resulting in a narrow particle size distribution. However, separating nanoparticles from larger particles during ACC processing is difficult. Most current technologies do not have such a separation mechanism.

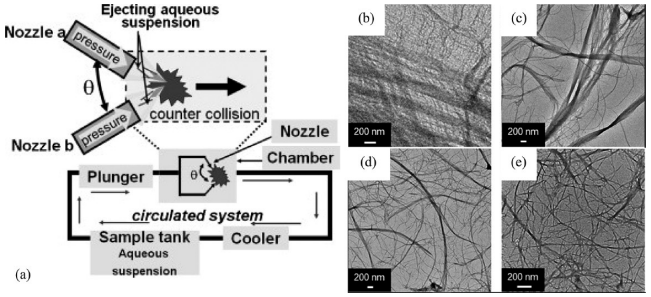

Figure 5. Sugino Machine Star Burst aqueous counter collision system (a). Reprinted from ref 87. Copyright 2014 with permission from Elsevier. TEM images of the CNFs at different cycle numbers: 5 passes (b), 10 passes (c), 40 passes (d), and 80 passes (e). Reprinted from ref 119. Copyright 2015 with permission from Elsevier.

Because the channel size is small (microscale in diameter), the starting materials are usually microcrystalline cellulose (MCC), ground cellulose, or pretreated pulp. The concentration of the suspension is usually lower than 2 wt %. The major work in ACC has been conducted by Kondo's research group. Kondo et al. explored the use of ACC to make CNFs from MCC,[87,120,121] rice straw[28] and bacterial cellulose.[88] The ACC process transformed the cellulose form from I_α to I_β, with tunable crystalline/amorphous ratios achieved by changing the processing conditions.[88] Because the ACC method produced CNFs with exposed hydrophobic surfaces, they were investigated as a potential *Pickering* emulsifier.[120,121] Jiang et al. also prepared CNFs with ACC from purified rice straw, with increasing weight factions yielding thinner nanofibrils.[28] More than 90% of the nanofibrils were smaller than 80 nm in diameter. The nanofibrillation yield more than doubled the yield of CNFs produced by the microfluidizing approach. The energy consumption of such a process was only 1/3 of the grinding process. There is one commercial/pilot scale producer of ACC-CNFs, which is Chuetsu Pulp and Paper, Japan.[122]

4.6. Ultrasonication. Ultrasound occurs in the spectral range of 20 kHz to 10 MHz and is produced by conversion of

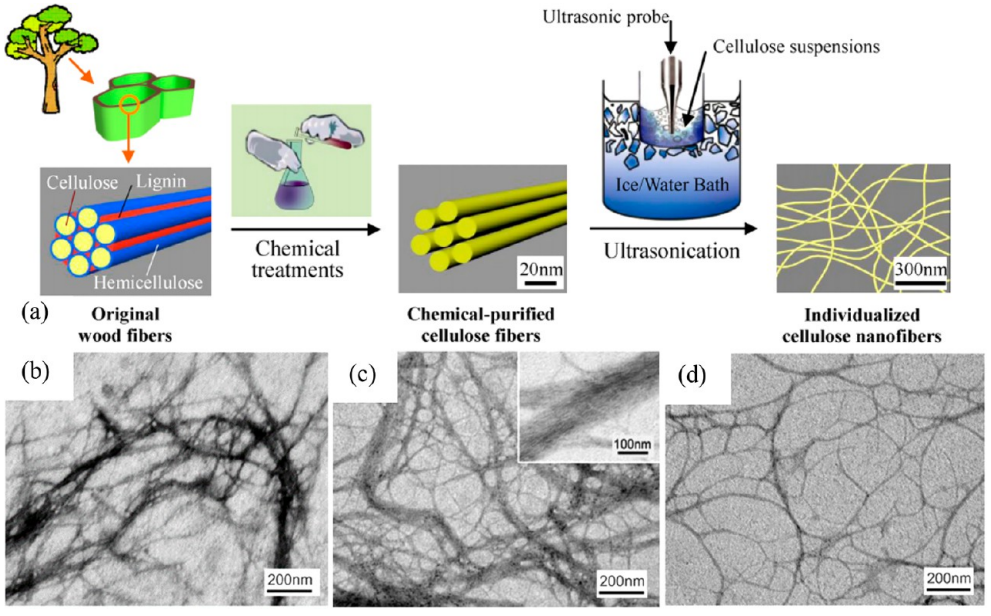

Figure 6. Schematic illustration of producing CNFs via ultrasonication with chemical pretreatments (a). TEM graphs of ultrasonication-generated CNFs with various power output: 400 (b), 800 (c), and 1000 W (d). Reprinted from ref 123. Copyright 2011 with permission from Elsevier.

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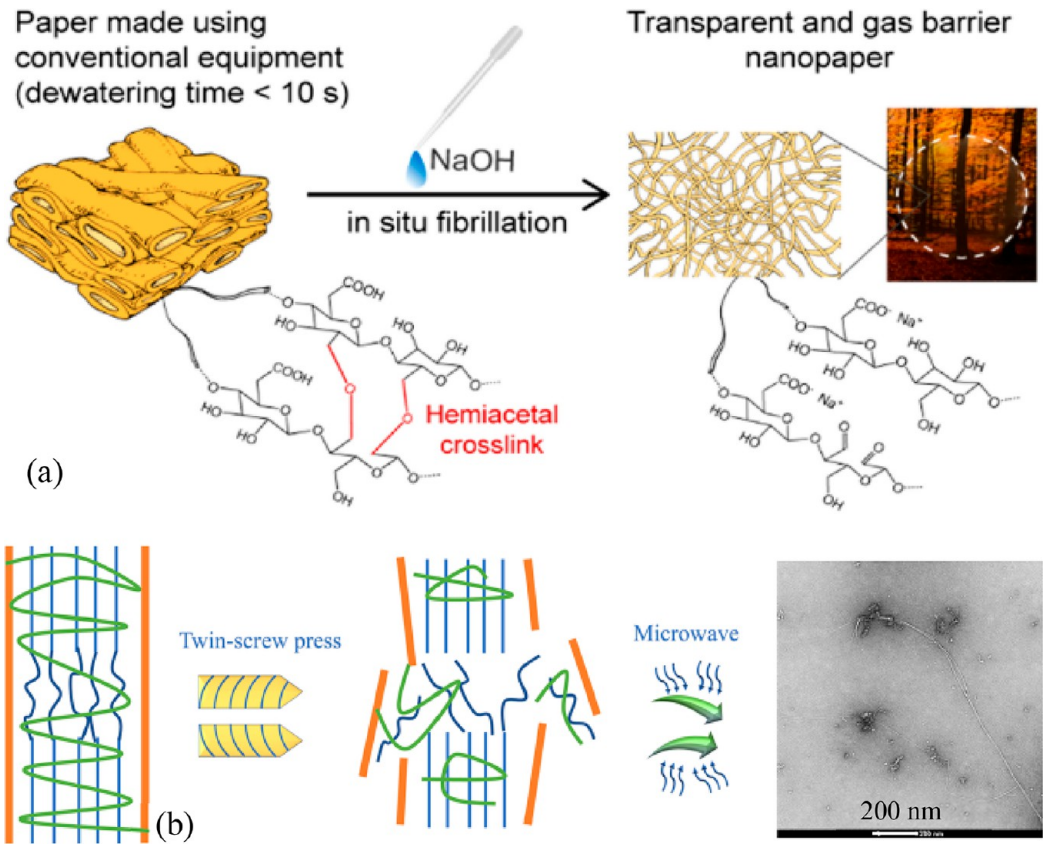

Figure 7. Schemes of producing nanocellulose by pH-induced self-fibrillation (a). Reprinted from ref 94 with permission. Copyright 2020 American Chemical Society. Twin-screw extrusion and microwave hydrothermal treatment (b). Reprinted from ref 43 with permission. Copyright 2019 American Chemical Society.

mechanical or electrical energy into acoustic energy. The strong oscillating power generated by the cavitation processes, produces powerful hydrodynamic forces that can facilitate the fibrillation of natural fibers into micro/nano fibers.[58,89−91,123,124] Ultrasonication can treat cellulose fibers to improve accessibility and reactivity of the cellulose during the fibrillation process as shown in Figure 6a.[125] Factors that have been demonstrated to affect the efficiency of fibrillation via ultrasonication include ultrasound power, time, temperature, fiber content in suspension, fiber size, and distance from the transducer, among others.[124] Chen et al. investigated the impact of ultrasonication on cellulose fibrillation of four different plant cellulose fibers.[89,123] The plant fibers were each chemically purified prior to sonication of the cellulose suspensions at 20−25 kHz to isolate the nanofibers. The ultrasonication treatment produce a modest degree of fibrillation, with fibrillation increasing progressively with the power applied.[89] The morphology of these CNFs produced via ultrasonication are shown in Figure 6b−d. Besides being a major method of producing CNFs, ultrasonication has also been applied as a pretreatment for producing nanocellulose.[124,126] For example, Wang et al. reported that ultrasonication facilitated the fibrillation of cellulose fibers during homogenization and resulted in a more uniform cellulose suspension after the combined treatment.[124] Additionally, ultrasonication has been used as a post-treatment to defibrillate individual nanofibers from TEMPO-oxidize cellulose fibers.[127]

4.7. Cryocrushing. Cryocrushing is well-known in the plastics industry, especially for the mechanical pulverizing of tough polymers such as polyolefins. Cryocrushing for natural fiber fibrillation has only recently been investigated.[93,128] During cryocrushing, the water in natural fibers is frozen rapidly upon immersion in liquid nitrogen. The cell wall can then be significantly fragmented by the rupture of ice crystals as the frozen fibers undergo mechanical grinding, resulting in the formation of CNFs.[5] A high yield (up to 89%) of CNF production was reported by Chakraborty et al. for cryocrushing of pulp fibers.[128] The resulting CNFs had aspect ratios ranging from 15 to 85. With a combined acid and alkaline pretreatments, the size of CNFs produced from cryocrushing can be reduced to 40 nm in diameter.[93] Cryo-crushed, fibrillated CNFs have exhibited a very significant reinforcing effect in PVA by more than tripling its tensile properties.[93] In addition to cryocrushing being employed directly to create CNFs, the technique has also been used as a pretreatment for manufacturing CNFs by conventional fibrillation methods.[5,129]

4.8. Other Methods. There are some other interesting methods for CNF fibrillation that have been less widely studied, but are worthy of attention. For example, Gorur et al. prepared nanopaper via *in-situ* fibrillation of paper using the process shown in Figure 7a.[94] Pulp fibers comprising conventional paper were pretreated by sequential TEMPO and periodate oxidation in water, which minimized the H-bonding and cross-linking among cellulose chains. Upon increasing the suspension's pH level, electrostatic repulsion among fibers was enhanced, leading to the self-fibrillation of pulp fibers into CNFs. Gao et al. made CNFs and CNCs from pea waste via a microwave hydrothermal treatment (MHT = 1.2 kW, 2.45 GHz, 120−200 °C), employing TSE pretreatment, as shown in Figure 7b.[43] The fibers produced exhibited

https://doi.org/10.1021/acs.biomac.1c00640
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high crystallinity, water retention capability, and surface area. However, the fibers generated appeared to display a large variation in particle size.

5. APPLICATIONS

Commercial applications of CNFs are generally driven by their potential to improve material properties with the added value of being derived from renewable natural resources. Features of CNFs such as high aspect ratio, nanoscale dimensions and high crystallinity have the potential to provide significant improvements in material strength and flexibility, as well as oxygen resistance. One limitation to the widespread adoption of CNFs is the energy costs associated with their production.[14] Several novel fibrillation methods have been reviewed that are capable of producing CNFs with features suitable to a variety of applications. The applications, CNF feedstock, production methods and mechanical properties of the products are discussed in the following sections. A summary of the film and polymer composite properties of nonconventionally fibrillated CNFs is provided in Table 2.

5.1. Films. The incorporation of CNFs has expanded the use of cellulose films beyond conventional paper applications to high performance material usage in electronics, energy storage, and water treatment.[135] The ability to manipulate the optical, mechanical, and thermal properties of CNFs has resulted in a wide range of functional nanomaterials. Several examples of nonconventionally fibrillated, CNF-film applications are given below.

The fibrillation method employed to generate CNFs can impact the strength and, in some cases, the thermal properties of the resulting films. Generally, CNF films generated from extrusion fibrillation are weaker to those produced from conventional methods regarding their tensile properties.[18] A lower degree of fibrillation of CNFs from extrusion, and a lower degree of dispersion of CNFs in water from their original high-solid-content paste were considered as the major reasons behind the weaker tensile performances of extrusion-fibrillation CNF films.[18] Ball milling has been used by both Abe et al.[130] and Deng et al.[34] to modulate the strength and transparency of CNF films. Abe et al. developed a continuous process to ball mill dried pulp in a highly concentrated (8 wt %) NaOH solution that yielded 20−50 nm diameter CNFs. The minimum milling time that could be employed to produce a smooth film was found to be 90 min. The resultant CNF film had a Young's modulus of 9.3 GPa. Optimization of the milling conditions could potentially produce even higher strength films, as the conditions used resulted in a partial conversion from cellulose I to II crystalline form. Li et al. utilized high intensity ultrasonication to extract long (>500 μm) CNFs from bleached hardwood kraft pulp and then used them to reinforce poly(vinyl alcohol) (PVA) films.[91] The advantage of using ultrasonication was that the fibrils retained their cellulose I crystal structure which resulted in stronger films (1.86 and 1.63 times greater tensile strength and Young's modulus, respectively) when compared to neat PVA.

Several investigators have evaluated the impact of fiber pretreatments prior to nonconventional fibrillation on the physical properties of CNF films. For example, Rol et al. were able to increase the modulus of CNF films obtained using an enzymatic pretreatment followed by TSE fibrillation to 15.4 GPa while consuming 60% less energy than required to produce TEMPO−CNFs.[18] In addition to greater strength, the enzymatic pretreatment combined with TSE fibrillation produced a film with higher transparency (89%) versus a CNF film (55%) produced merely from TSE fibrillation. The effect of chemical treatments during nonconventional fibrillation on CNF film properties have also been extensively investigated. Specifically, Deng et al. utilized ball milling in the presence of hexanoyl chloride to produce hydrophobic CMF films that were less sensitive to moisture.[34] Indeed the acylated-CMF films had a lower water vapor permeability (WVP) ($<1 \times 10^3$ g·mm/(m^2·day·atm)) compared to cellulose films (13×10^3 g·mm/(m^2·day·atm). Further, acylated films had a 162% increase in tensile strength and a 1083% increase in elongation at break compared to CMF films without acylation. Finally, increases in both the extent of acylation and the milling time led to increases in optical transparency, as seen in Figure 8a. Other interesting CNF film functionalities that have been imparted through chemical treatments include antimicrobial characteristics via cationization[23] and fire retardancy through phosphorylation.[19,131]

CNF films derived from agricultural residues processed via nonconventional fibrillation methods have been widely investigated. Specifically, Dufresne et al. utilized cryocrushing and a blender to fibrillate sugar beet pulp.[5] The resulting CMFs were subsequently cast into films in which the native pectin acted as a binder. It was determined that the tensile modulus of the films increased (up to 3 GPa) in proportion to the duration of the mechanical treatment of the pulp. Cryocrushing was shown to generate individual microfibrils and to support the subsequent formation of a network of CMFs within the material. It is noted that the ability to isolate individual microfibrils is likely facilitated by the low pectin content of the feedstock. Chen et al. employed ultrasonication to isolate nanofibers from four different agricultural waste materials (wood, bamboo, wheat straw, and flax) and to cast them into films.[89] The CNF properties yielded by the purification−ultrasonic pretreatments made them suitable for nanocomposites, filtration media and optically transparent films. Chemical treatment resulted in a higher α-cellulose content in the product. Specifically an increase of 30% over the starting value for the wood, bamboo, and wheat straw feedstocks was observed. A similar increase in α-cellulose content was not observed for flax, which had a high initial content of 88%. The increased crystallinity of the CNF products yielded improved thermal properties of the resultant films (thermal degradation at >330 °C compared to 210 °C for untreated fibers).

5.2. Polymer Composites. Inclusion of CNFs in composites can have a significant impact on the material properties (especially mechanical properties) of the resultant materials. An overview of various CNF−polymer composites and their associated properties is provided Table 2. In one study, Boufi and Chaker produced CNF/acrylic latex composites using a conventional high-speed blender over a range of CNF contents (1−15 wt %).[26] It was observed that at 10 wt % CNFs, the tensile strength and modulus of the composite were approximately 10 and 125 times higher than those of the neat latex, respectively. Fourati et al. observed increases in the tensile strength and Young's modulus when incorporating CNFs generated via an extrusion technique into TPS composites.[104] Li et al. produced CNFs using ultrasonication for use in PVA composites.[91] CNF contents of 0, 2, 4, 8, and 12 wt % were employed. Progressively increasing mechanical performance of the composite PVA films was observed as the CNF content increased. An alternate means of

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

Table 2. Applications of CNFs from Nonconventional Production Methods and Their Film and Composite Performance

application form	feedstock	pre/post-treatment	fibrillation methods	product formation	mechanical properties			ref
					tensile strength (MPa)	tensile modulus (GPa)	breaking strain (%)	
single CNF films	refined cellulose fiber	TEMPO oxidization	extrusion (1 pass)	filtration, drying	41.2 (1.0)[o]	1.4 (0.1)	0.4 (0.1)	18
	refined cellulose fiber	enzyme (fibercare R)	extrusion (7 pass)	filtration, drying	33.9 (9.5)	15.1 (0.4)	0.6 (0.2)	18
	Eucalyptus bleached kraft pulp	refined, cationization (EPTMAC)[l]	extrusion (7 pass)	filtration, drying	72 (2.9)	7.3 (1.0)	N.A.	23
	refined *Eucalyptus* bleached kraft pulp	phosphorylated (DS = 0.1−0.2)	extrusion (7 passes)	sheet forming, vacuum drying	100	14	N.A.	19
	sugar cane bagasse fibers	enzyme/high intensity sonication	planetary ball mill	casting, evaporating	61 (3)	7.4 (1.0)	1.1 (0.2)	58
	softwood pulp	alkaline	planetary ball mill	neutralized wet sheets (dried hydrogels)	100 (4)	9.3 (0.4)	2.4 (0.2)	130
	wood pulp	homogenization, hexanoyl chloride	planetary ball milling	casting, evaporation	140 (7)	N.A.	21.3 (1.5)	34
	ramie	DES[k]	planetary ball milling	casting	98.01 (1.8)	2.75 (0.01)	7.7 (1.1)	51
	bleached birch kraft pulp	oxidation, oven drying	PFI milling	vacuum filtration	114.5	11.2	10.6	49
	Triodia pungens	delignification, acid	agitator ball milling	filtration and molding	65 (2.5)	1.8 (0.3)	9 (1)	81
	sugar beet pulp	chemical treatment, homogenization	cryocrushing	casting, evaporation	N.A.	3.2	N.A.	5
	triticale straws	delignification, Bleaching, TEMPO	blending	casting	33	N.A.	∼10	27
	rice straw, cellulose fibers	delignification, bleaching	ACC[n]	ultrafiltration/air drying	141	3.94	16.5	28
	bagasse fiber	delignification, refining, enzyme	ultrasonication	casting	∼63	∼7.5	∼1	58
	bleached kraft pulp	oxidation	pH-induced fibrillation	sheet forming	184	5.2	4.6	94
CNF/TPS[a](15/85)	kraft pulp	TEMPO oxidation	extrusion	compounding and molding	∼7.5	∼0.2	∼13	104
CMF/HEC[b] (20/80)	dissolved pulp	none	extrusion	hot pressing	∼16	∼1.4	∼1.1	98
CMF/PP[c]	wood saw dust	DES	extrusion	hot pressing	∼17	∼1.1	∼2.5	71
CMF/MAPP[d]/ CPPA[e]/PP (30/4/3/63)	unbleached kraft pulp	refining	extrusion	compounding and molding	72	4.6	3.8	99
CMF/MAPP/PP (50/6.7/43.3)	unbleached kraft pulp	refining	extrusion	compounding and molding	66	5.3	3.2	96
CMF/MAPP/$CaCO_3$/HDPE[f] (10/4/1/85)	bleached kraft pulp	refining and acetylation	extrusion	compounding and molding	56 (0.8)	3.46 (0.11)	3.2 (0.1)	97
CMF/MAPP/CPPA/HDPE (20/6/4/70)	bleached kraft pulp	refining	extrusion	compounding and molding	45 (0.4)	3.5 (0.1)	2.5 (1.1)	100
CNF/Paper (30/70)	corn cob cellulose	phosphorylation	ball milling	casting	∼28	N.A.	∼2.3	131
CNF/MAPP/CPPA/PP (30/12/9/49)	bleached kraft pulp	refining	bead milling	compounding and molding	59.6 (0.6)	4.09 (0.04)	4.5 (0.1)	101
CNF/Starch (0.5/99.5)	bleached kraft pulp	urea	colloid milling	casting	∼19	N.A.	∼3.3	132
CNF/PCL[g] (0.5/99.5)	CMF	chloride	ball milling	casting	∼43	∼0.3	∼1100	133
CNF/PVA[h] (10/90)	kraft pulp	none	cryocrushing	casting	102	7.4	N.A.	93
	rutabaga	alkaline, acid	cryocrushing	casting	178	10.1	N.A.	93
	flax fiber	alkaline, acid	cryocrushing	casting	76	6.1	N.A.	93
	hemp fiber	alkaline, acid	cryocrushing	casting	111	9.8	N.A.	93

https://doi.org/10.1021/acs.biomac.1c00640
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Table 2. continued

application form	feedstock	pre/post-treatment	fibrillation methods	product formation	mechanical properties			ref
					tensile strength (MPa)	tensile modulus (GPa)	breaking strain (%)	
	MCC[i]	none	ultrasonication	casting	~95	~5.2	N.A.	90
	PCF[j]	none	ultrasonication	casting	~110	~5.2	N.A.	90
	RCF[k]	none	ultrasonication	casting	130	6.8	N.A.	90
CNF/PVA (4/96)	bleached kraft pulp	alkaline	ultrasonication	casting	~35	~0.1	N.A.	91

[a]Thermoplastic starch. [b]Hydroxyethyl cellulose. [c]Polypropylene. [d]Maleic anhydride polypropylene. [e]Cationic polymer using primary amine. [f]High-density polyethylene. [g]Polycaprolactone. [h]Poly(vinyl alcohol). [i]Microcrystal cellulose. [j]Purified cellulose fiber. [k]Regenerated cellulose fiber. [l]Glycidyltrimethylammonium chloride. [m]Deep eutectic solvent. [n]Aqueous counter collision. [o]Values in parentheses are standard deviation.

incorporating CNFs into composites is to perform in situ fibrillation of pulp fibers during extrusion. Specifically, Suzuki et al. produced CMF/MAPP/CPPA/PP composites with three different CMF contents (30, 40, and 50 wt %) via *in-situ* fibrillation.[99] CPPA is a cationic polymer using a primary amine which acts as an effective coupling agent. The CMFs were produced by fibrillating pulp fibers with polymer powders during chilled extrusion. Yano et al. produced CMFs via extrusion for addition to polyolefin composites. The resultant composites displayed improved thermal properties, such as higher heat deflection temperature (up to 122 °C)[96] and lower coefficient of thermal expansion (down to 54 ppm/K).[97] It is noted that inferior filler−matrix interactions remain a challenge in the production of CNF or CMF composites.[47] A number of research efforts have been made to incorporate surface modification into fibrillation processes to generate an improved dispersion of CNFs within hydrophobic polymer matrices. For example, Suzuki et al. fibrillated bleached kraft pulp using TSE with the addition of CPPA or MAPP coupling agents, before re-extrusion with PP to generate composites with an improved tensile strength and modulus.[99] Deng et al. functionalized and generated fibrillated CNFs in a single step by ball milling CMFs in the presence of hexanoyl chloride.[133] The resulting fibers had strong interfacial adhesion with a polycaprolactone (PCL) matrix.

5.3. Aerogels. CNFs are well suited as source materials for hydrogels and aerogels because of their inherent hydrogen bonding, electrostatic interactions, and fibril structure with high aspect ratio. Fibrillation methods for preparing aerogels are largely selected based on their reduced energy or cost, as opposed to providing specific surface modification or reduction of surface charge advantages.[136] However, some researchers have investigated the direct preparation of nanocomposite CNF-based aerogels to mitigate the need of multistep post processing and to efficiently add functionality throughout the aerogel network. For example, Zhang et al. prepared ultralightweight CNF-based aerogel microspheres via ultrasonication for use as suspension microreactors in tailored separation/extraction applications.[134] Softwood pulp was used to prepare TOCN suspensions, and ultrasonication was used to make a homogeneous mixture of small uniform droplets. The aerogel microspheres were isolated via freeze-drying (Figure 8b and c). Decreasing ultrasonication time from 6 to 2 min yielded more compact microsphere structures (the diameter was reduced from approximately 7 to 2 μm), while increasing ultrasound time resulted in a more porous morphology. The use of a covalent cross-linker (polyamide-epichlorohydrin) drastically increased the aerogel stability in harsh environments and facilitated subsequent reusability without decreasing removal efficiency. The CNF-based aerogels were able to absorb 120 $g \cdot g^{-1}$ of water and to remove 93% of phenol and 82% of Cu^{2+} from solution.

5.4. *Pickering* Emulsifiers. A Pickering emulsifier refers to a solid particle which is capable of stabilizing oil droplet in water by accumulating at the interface of the two liquids.[121] *Pickering* emulsion stabilization was achieved using CNFs prepared by Yokota et al. via ACC approach.[121] It is noted that ACC−CNFs are typically more hydrophobic than fibers produced by physical grinding or pulverization because of the selective cleavage of the hydrophobic *(200)* planes in native crystalline cellulose during ACC treatment.[121] Therefore, ACC-produced fibrils have pronounced amphiphilic properties and can be used as emulsifiers without the addition

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

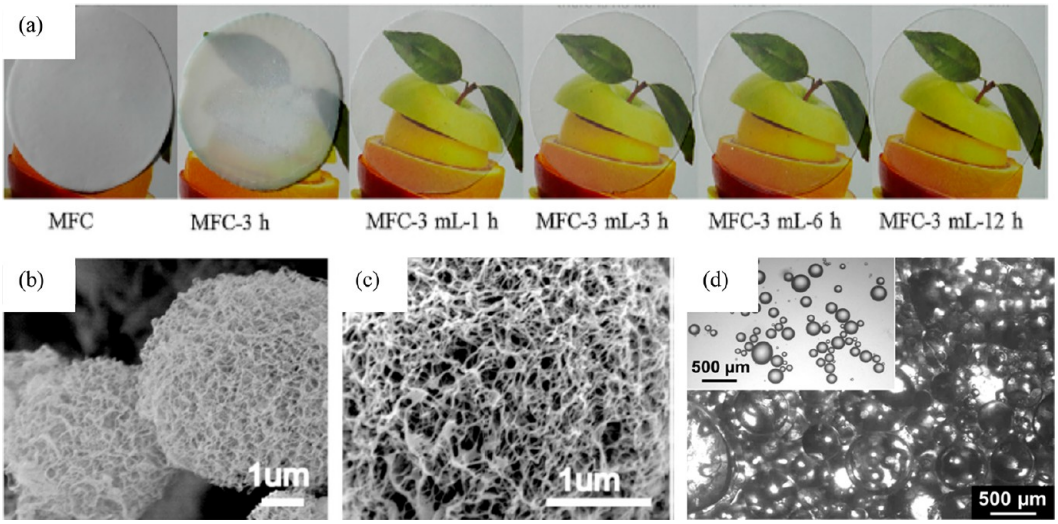

Figure 8. Effect of milling time (h) and hexanoyl chloride dose (mL) vs CMF film transparency (a). Reprinted from ref 34. Copyright 2016 with permission from Elsevier. SEM images of TEMPO-oxidized cellulose nanofiber aerogel microspheres with 6 min of ultrasonication (b) and higher magnification image reveals approximate diameter of nanofiber bundles to be dozens of nanometers (c). Reprinted by permission form Springer Nature ref 134. Copyright 2017. Microscopic images of Pickering emulsions in cyclohexane stabilized by ACC−CNFs observed 1 h after sonication (d). Reprinted from ref 121. Copyright 2019 with permission from Elsevier.

Table 3. Summary of the Nonconventional Fibrillation Methods Covered in This Review

nonconventional fibrillation method (mechanism)	energy consumption (kWh/kg)	benefit	challenge
extrusion (compression and shear)	2−6 (pretreatment)	1. Final CNFs in high solid content. Lower transportation cost. 2. Easy modification of screw profile for process optimization. 3. No clogging during operation. 4. Industrial scalable. 5. Potentially low energy consumption.	1. Low production rate (based on lab study with 16 mm-diameter screws). 2. Fibers are less consistent in one-pass extrusion.
ball milling (compression and shear)	unknown	1. No clogging during fibrillation. 2. Dry nanofibers potentially achievable.	1. Noncontinuous process. 2. Fibers are inconsistent.
blending (cutting and shear)	11−15 (pretreatment)	1. Low capital investment (lab scale).	1. Energy intensive. 2. Final CNFs with low solid content. 3. Fibers are inconsistent.
steam explosion/ (fibril splitting by instant vapor expansion)	unknown	1. Industrial scalable. 2. Dry nanofibers potentially achievable.	1. Inconsistent fiber quality. 2. Noncontinuous, multiple-step process. 3. Potential fiber degradation from elevated pressures and temperatures.
aqueous counter collision (cavitation, shear)	15 (pretreatment)	1. High yield. 2. Potentially less tool wear.	1. Requiring small (<150 μm) feedstock. 2. Energy intensive.
Ultrasonication (cavitation, hydrodynamic shear)	40−48 (pretreatment)	1. Low capital investment (lab scale).	1. Noncontinuous process. 2. Energy intensive.
cryocrushing (pulverization, splitting, shear)	unknown	1. Dry fibers potentially achievable.	1. Noncontinuous process. 2. Most fibers are not in nanoscale.
pH-induced self-fibrillation (electrostatic repulsion)	unknown	1. No special device is needed as the process involves no primary mechanical force.	1. Involvement of extensive and toxic chemical pretreatments.
microwave hydrotherm (hydrolysis)	unknown	1. Low capital investment (lab scale).	1. Fibers are inconsistent in quality.

of a surfactant. The emulsifier capabilities of the ACC−CNFs was evaluated using a variety of solvents. It was determined that they formed stable oil/water Pickering emulsions, containing *n*-octane, cyclopentane, *n*-decane, or cyclohexane (Figure 8d). No emulsion was observed in *n*-hexane, a finding which differed from the work of Tsuboi et al.,[137] who observed *n*-hexane emulsification when employing ACC−CNFs derived from wood and bamboo kraft pulp fibers.

6. CONCLUSIONS AND FUTURE WORK

As CNF research continues to evolve in both industry and academia, the industrial-scale production of CNFs at low cost is becoming more urgent. Producing CNFs via nonconventional fibrillation methods results in materials that exhibit similar attributes to those produced via conventional methods. Certainly challenges and opportunities coexist for scale-up and application of CNF materials using nonconventional fibrillation methods, which are summarized in Table 3.

https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

Importantly, there is no single means to measure the degree of fibrillation of CNFs. In fact, the term "degree of fibrillation" itself lacks a formal definition, and there is no established or direct term to encapsulate all aspects that can be described by fibrillation, such as fibril length and diameter, internal versus external fibrillation, process yield, etc. The quality index is a more accurate way of presenting and comparing the CNF properties, however, merely valid for pretreated fibers. A more inclusive method is needed for TOCN or other CNF suspensions containing additives, where the turbidity measurements will be disturbed.

Extrusion fibrillation is a promising methodology for producing CNFs from lignocellulosic feedstock. It has been shown that the size of the equipment affects the yield of fibrillation, but not the degree of fibrillation, a fortunate outcome that limits the need for large capital investment in research and development efforts. Pretreatment appears to be a prerequisite to obtain highly fibrillated CNFs from pulp fibers using TSE, although the work of Ho et al.[77] may indicate otherwise. It is recommended that future research investigate the use of more biobased feedstocks other than wood and the use of cost-effective pretreatment methods. Co-extrusion of pulp fibers and polymers has been show to generally result in the production of a combination of CNFs and CMFs, with the latter being the major portion. However, while complete nanoscale dispersion of fibers may be a laudable goal, it may not be necessary for polymer composite applications as the mechanical properties of a host of polymer/fiber reinforced materials have been shown to significantly improve with *in-situ* fibrillated CMFs.

Employing ball-milling and blending to fabricate CNFs has not be extensively investigated to date, a surprising fact given the multitude of papers which have utilized these techniques for producing other nanomaterials. Variations in processing speed, power, and time, along with the use of additives, have produced a wide array of CNF properties via these techniques. Indeed, thermal stability, crystallinity, mechanical properties, and morphology have been observed to vary greatly. More work is needed to understand and optimize blending as a straightforward method of producing CNFs. Additionally, development of new ball-milling and blending strategies which more efficiently utilize the mechanical energy input would provide more efficient fibrillation.

Steam explosion provides an inexpensive and green solution to producing CMFs/CNFs from lignocellulosic biomass. However, caution must be taken when utilizing steam explosion as depending on the process conditions employed, it may expose cellulose to temperatures and pressures that can result in degradation. To mitigate the amount of cellulose degradation, steam explosion should be conducted at elevated temperatures and pressures in repeated cycles of shortened time periods. Lower temperature and pressure steam explosion has proven effective for pretreating cellulose for subsequent mechanical homogenization. In addition, acidic or alkaline media may be employed to promote separation of fibers during the rapid decompression process. However, solely employing water as the liquid medium where possible is preferable in order to remain environmentally friendly, maintain low cytotoxicity levels and simplify the process.

The aqueous counter collision process is an innovative and environmentally friendly method of producing CNFs which uses only water and lignocellulosic feedstocks. However, the process is energy-intensive due to the need to generate the high-pressure and high-speed water jet, which is guided to produce the various shearing, impacting and cavitating actions that fibrillate fibers. To reduce the energy requirements of these systems, and to make the process more economically attractive, chemical or enzymatic pretreatments are recommended. Additional work is also recommended to explore the effects of the interaction chamber configuration on the morphology and size distribution of the resulting CNFs and on the energy efficiency of the system.

CNFs produced from either ultrasonication or cryocrushing have not been as thoroughly characterized as those from other nonconventional fibrillation methods. However, it appears that the application of either technique on their own may not be sufficient to produce highly fibrillated and uniform CNFs. The majority of fibers produced by cryocrushing are on the micron scale. Additionally, both methods are energy-intensive. Therefore, there are limited studies available in literatures using these fibrillation techniques for producing CNFs. The use of ultrasonication and cryocrushing as pretreatments should be more thoroughly investigated and analyzed to verify their positive effects in following fibrillation.

The drive to develop materials and processes to support a circular economy is increasing. CNFs derived from nonconventional fibrillation methods have been investigated for various applications, such as films, polymer composites, aerogels, *Pickering* emulsifier, etc. The range of applications utilizing CNFs is attributable to the natural abundance of its feedstock, along with its sustainability. It is hoped that continued efforts will be invested in developing novel and efficient fibrillation techniques to further expand the use of CNFs.

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https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. L.W.: Conceptualization; writing, original draft; writing, review and editing. K.L.: Writing, original draft; writing, review and editing. K.C.: Writing, original draft; writing, review and editing. S.M.: Writing, original draft; writing, review and editing. M.E.L.: Writing, original draft; writing, review and editing. X.Z.: Writing, original draft; writing, review and editing. B.D.: Writing, original draft; writing, review and editing. J.W.: Writing, original draft; writing, review and editing. Y.H.: Writing, original draft; writing, review and editing. D.N.: Writing, review and editing. D.A.J.: Writing, review and editing. C.C.W.: Writing, review and editing. S.O.: Conceptualization; writing, review and editing; supervision; funding acquisition. D.J.G.: Conceptualization; writing, original draft; writing, review and editing; supervision; funding acquisition.

Notes

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■ ACKNOWLEDGMENTS

Authors from Oak Ridge National Laboratory (ORNL) are supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DEAC05-00OR22725 with UT-Battelle LLC. Authors from University of Maine are grateful for the funding support from UT-Battelle LLC with the U.S. Department of Energy under contract DEAC05-00OR22725 (subcontract 4000174848). Authors are grateful to Olivia Shafer from ORNL for proof reading the manuscript before submission.

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https://doi.org/10.1021/acs.biomac.1c00640
Biomacromolecules 2021, 22, 4037−4059