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Commercialization of Cellulose Nanofibril (CNF) and Cellulose Nanocrystal (CNC): Pathway and Challenges

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Abstract

The status of pilot-scale production methods for cellulose nanorods or nanocrystals and the 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-0xyl (TEMPO) grade of cellu—lose nanofibrils are discussed. Both products appear to be poised for scale-up when markets develop, but there are a number of issues that need to be addressed. This chapter outlines concepts for conversion to continuous processes and other issues and concerns that need to be resolved for investments in commercial-scale pro-duction facilities. For large-scale production of cellulose nanocrystals, topic items include site selection, materials of construction, diafiltration, and acid recovery. For production of TEMPO grade fibrils, concerns include site selection, materi-als of construction, reaction kinetics relative to plant design, shear sensitivity of the treated pulp, and TEMPO recovery. Drying concerns are a significant problem in that currently practiced methods are energy intensive and do not provide readily dispersible nanoscale particles.

Keywords commercialization; scale-up and Production; cellulose nanocrystal; cellulose nanofibril

List of Abbreviations

13C CPMAS	carbon 13 cross-polarization magic angle spinning solid-state NMR
13C NMR	carbon 13 nuclear magnetic resonance spectroscopy
	CNC cellulose nanocrystal, used in reference to the 64% sulfuric acid isolation method
CNF	cellulose nanofibrils; used in reference to all high aspect ratio cellulose nanoparticle shapes including linear, branched
CNR	cellulose nanorod; used in reference to all short aspect ratio particles isolated by any method that produces rod-shaped

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	particles, as opposed to the string»shaped and longer aspect ratio particles generally referred to as fibrils
DMF	dlimethylformamide
DMSO	dimethylsulfoxide
DP	degree of polymerization
FPL	Forest Products Laboratory: United States Department of Agriculture, Forest Service Research and Development
meq g^{-1}	milliequivalents per gram. This is used instead of the more common millimoles per gram since a mole is not well defined for acid functional groups on a polymer
mt	metric ton
PVC	polyvinyl chloride
R&D	Research and Development
RO	reverse osmosis quality water
TC	terminal cellulose»synthesizing complex
TEMPO	2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl. This is a catalytic oxidation mediator that selectively oxidizes the primary alcohol (C6) group of sugars
TMP	thermomechanical pulp
TOCN	TEMPO-oxidized cellulose nanofibril. Reference to the nanofibrils produced after oxidation by TEMPO and TEMPO derivatives
UNS	United Alloy Numbering System
WAXS	wide angle X-ray scattering
WRV	water retention value

23.1 Introduction

23.1.1 Cellulose

Cellulose has a long history of human use as a textile, Cotton is nearly pure cellulose, and linen, a textile fiber produced from the flax plant, is also primarily cellulose. Cellulose also has a long industrial history as the wood pulp used in paper and the textile polymers acetate (cellulose acetate) and rayon (regenerated cellulose). These last two polymers, which have been in industrial use for halfa century, also demonstrate some of the physical properties of interest and value in cellulose nanomaterials. Cellulose acetate is used in LCD displays because of its optical clarity. Rayon as a high tensile fiber was the primary polymer used as the reinforcing cord in vehicle tires for four decades and is still used for this purpose by some manufactures.

Cellulose nanoparticles are products of the plant polymerization process and inherit this history of industrial applications of cellulose. They also have a variety of different and improved properties that scientists and engineers the world over are working on to incorporate into new and valued products. These include superior strength and rheological properties, and additional possibilities for use in liquid crystal-like applications, piezoelectric applications, and barrier film applications.

Cellulose is a linear polymer of the six-carbon sugar glucose and is a structural component of the cell wall of nearly all plants. Starches (amylose and amylopectin) are also plant polymers made up of glucose monomers [1]. Glucose has the molecular formula $C_6H_{12}O_6$. Cellulose and starches have the molecular formula $C_6H_{10}O_5$. The polymers have formed by dehydrating glucose, removing one molecule of water per molecule of glucose. The three polymers differ in the way in which glucose molecules bond to produce the polymer [1] and this is the primary difference between cellulose, a structural polymer that is only degraded by a few fungi and bacteria, and the starches that are a universal food storage polymer consumed and metabolized by nearly all forms of life. In cellulose and the starches, the glucose molecules bond into a linear chain as acetals. Initially, the alcohol on C-5 of the glucose attacks the aldehyde at C-1 forming a hemiacetal as a six-membered ring structure. This is the common form of glucose. The OH group of the hemiacetal then bonds to the C-4 carbon of another glucose to form the acetal and the polymer [1]. This second bond results in the loss of one molecule of water per monomer of glucose. That acetal bond can form in one of two configurations. The α- form is the polymerization bonding found in amylose and amylopectin [1]. The β- configuration is the polymerization onding in cellulose. In addition to the polymeric chains of 1,4- α- glucopyranose, amylopectin contains side chains bonded to the C-6 carbon of another chain, giving a branched structure [1]. The α- acetal of amylose and amylopectin is easily hydrolyzed by enzymes to recover the glucose monomers and this process is common in converting starch to glucose, which provides the energy needed for body functions, The [3-acetal is not readily hydrolyzed by animals and is used by plants as a structural polymer helping to support cell walls and the structural elements of stems, leaves, and roots.

The cellulose polymer is produced in plants by an organelle referred to as a terminal cellulose-synthesizing complex (TC) [2]. The size and form of the TC changes from one plant phylum to another, but most terrestrial plants have rosettes, a circular arrangement consisting of six individual cellulose-synthesizing units. Each of these units produces 6 chains of cellulose giving 36 total chains extruded into a filament of about 2nm diameter. The clusters of chains collect together forming recognizable elements within the plant cell wall, elementary fibrils at 7-9 nm (ramie) [3] or 5-10 nm (wood) [4], and microfibrils at 15-25 nm diameter [3, 5]. In addition to cellulose, most plants also incorporate two other polymers in the cell wall. Hemicellulose is a mixture of other polysaccharides — sugar-based polymers [6]. But with the hemicelluloses, the sugars are varied in each type of polymer and, in many cases, the hemicellulose polymer is branched similarly to amylopectin. While cellulose is a high-strength polymer and seems to provide the reinforcing element in plants, hemicellulose is far less strong and appears to provide more of an interface holding fibrils together and helping cellulose adhere to lignin, the third major plant polymer [7, 8]. Lignin is a cross-linked phenolic polymer that is often thought of as the glue holding the other polymers together and providing the stiffness needed for plant cell walls. Most cellulose nanomaterials are made from sources where hemicellulose and lignin have been removed, but nonetheless, their presence in the initial plant cell wall dictates some of

the properties of the cellulose nanomaterials that can be isolated. In particular, the presence of hemicellulose and lignin prevent extensive crystallization of cellulose, constraining the cellulose crystals to the specific size common in that particular plant species. It also appears that crystal formation dictates the smallest fibril size that can be isolated from a particular species [4]. More detail on cellulose synthesis is beyond the scope of this chapter, which is focused on production of the various cellulose nanoparticles. The point of this brief summary on the cell wall polymers is that the size and shape of the rosette and the way in which the plant organizes cellulose, hemicellulose, and lignin in the plant cell wall dictate the size of both cellulose crystals and the finest of the cellulose nanofibrils (CNFs), A large element of process control - reproducible particle size and shape — is controlled by the choice of cellulose source. While considerable variations in cellulose nanocrystal (CNC) size have been reported, the uniformity in size for a given raw material is very high relative to the wide ranges in particle sizes typically obtained in producing other nanoparticles such as carbon nanotubes.

23.1.2 Cellulose Crystals

As stated in the previous section, cellulose crystals appear to be a controlling feature for the size of both CNCs and high-grade chemical fibrils such as the 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TEMPO) grade. Specifically, the diameter of CNC from any particular cellulose source and the diameter of the TEMPO fibrils from the same source are similar and typically within the variability of these measurements. It was cellulose crystallinity that led to the initial discovery of CNCs in 1949 [9], but cellulose crystallinity persists as one of the most controversial of topic areas within the broader field of cellulose chemistry. Unfortunately, CNCs as a form of cellulose have inherited the uncertainties and ambiguities of the science,
From a chemical perspective, a crystal is a solid material with a repeating order of atoms or molecules. When these conditions are satisfied, the material scatters or diffracts short-wavelength probes, providing an interference pattern that relates by Fourier transform to the position of the atoms and their repeating arrangement in the solid. X-rays, electrons, and neutrons all provide short-wavelength light beams or particle beams that match the atomic spacing in crystals and can be used in crystallography. Single crystal diffraction is a powerful tool used by chemists to determine the exact arrangement of atoms in a molecule. Powder diffraction methods are less powerful, but readily demonstrate that a material is comprised of crystals and can determine the crystal unit cell dimensions (the basic unique unit of atoms or molecules that repeats in the crystal). X-ray powder pattern methods had demonstrated the repeating unit of the cellulose crystal by 1921 [10].

Cellulose also forms different crystal morphologies when treated with strong alkali or is dissolved and precipitated as in rayon. The crystal form of these latter two are referred to as cellulose II, to distinguish this form from native cellulose, which is delineated as cellulose I. In addition to cellulose I and II, cellulose III is formed from ammonia solutions, and cellulose IV from high-temperature treatments of cellulose II [11].

Unfortunately, the elements in cellulose — carbon, hydrogen, and oxygen - do not scatter X-rays very strongly; the crystals are very small and they are embedded in a noncrystalline or amorphous phase. All of these factors contribute to very poor diffraction data and a very poor understanding of what the cellulose crystal really is. While the basics of the cellulose crystal have been known since 1921, many details were not sorted out for decades. One unexpected problem was reported in 1956 when Marrinan and Mann determined that there were two forms of cellulose I detectable using infrared spectroscopy [12]. They labeled the two types as cellulose IA and cellulose IB with type A found in algae, Valonia ventricosa, and the cellulose extruded by Acetobacler bacteria. Type B was found in cotton, ramie, and linen. Subsequently, Honjo and Watanabe evaluated the crystal structure of the cellulose in Valonizz using electron diffraction [13] and observed differences from the standard cellulose X-ray powder diffraction and proposed different unit cell dimensions and a different space group. This was confirmed in 1974 with electron diffraction measurements for cotton, ramie, Acetobacter xylinum and Valonia [14]. These differences were more fully explained by Atalla and Vanderhart in 1984 using solid-state 13C NMR (carbon 13 nuclear magnetic resonance spectroscopy) [15]. Native cellulose is a mixture of two crystal morphologies, Using spectral subtraction methods, they proposed 13C CPMAS (carbon 13 cross-polarization magic angle spinning solid-state NMR) spectra for two "pure" forms, cellulose Ia, which was the predominate form in the cellulose from Valonia and Acetobacter, and Ifl, which was the predominate form in cotton and ramie. They estimated Valonia and Acetobacter at 60-70% cellulose Ia and cotton and ramie at 60-70% cellulose Ifl. With the discovery that the algae Glaucocystis produce nearly pure cellulose Ia [16], and cellulose collected from tunicates, a group of marine animals in the subphylum Tunicata, is nearly pure cellulose Ib [17], it became possible to more clearly identify these two forms. In perhaps the best crystallographic data obtained to date, using both X-ray and neutron scattering, these two forms have been resolved [18, 19] but still lack sufficient data to fully resolve the positions of all atoms in the unit cells.

Although X-ray crystallography tends to be the standard method to define crystals, it was not the method that first detected two forms; that was IR [12], or the method that teased out the composition of Ia and Ifl; this was accomplished using solid state 13C NMR [15]. Cellulose crystallinity is a subset ofthe overall problem in defining cellulose crystals. Crystallinity is defined as the fraction of cellulose in the crystalline form, and in order to determine crystallinity all crystalline forms and the amount of amorphous cellulose need to be determined. In addition to several X-ray scattering methods [20, 21], there are also techniques for determining cellulose crystallinity using Raman, infrared, and solid-state NMR spectroscopies [22]. Furthermore, there are often several proposed methods using each spectroscopic instrument, and the values that all of these methods provide for the percentage of cellulose that is crystalline often differ substantially. As an example, Terinte et al. compared outcomes from five different X-ray methods used for determining crystallinity. For Avicel PH-101, the estimates ranged from 37% to 93% [21]. Restricting the measurement to the Ruland method and a peak deconvolution method, the results were clustered between 54% and 78%. These

methods attempt to account for peak heights with an estimate of the amorphous component based on either a direct X-ray scattering measurement of an amorphous cellulose sample, or a theoretical amorphous background. The choice of this amorphous background is the biggest source ofdifferences in these estimates.

The outcome of decades of science is that cellulose crystallinity as currently practiced is not a standard method; cellulose crystallinity is not well defined, and the numbers provided by the different methods vary tremendously and cannot be relied on. At present, the shape of the cellulose crystal is distinguishing, a rod-shaped particle with an aspect ratio between 10 and 20. The incremental strength of the crystal has yet to be utilized and a distinction between highly crystalline and less crystalline particles is not currently critical. Should scientists working on cellulose nanoparticle-reinforced composites identify methods to obtain the huge surface bonding needed to utilize the full strength of these particles and they prove to have higher composite strength or modulus than similar composites containing amorphous cellulose reinforcement, a real definition ofwhat constitutes a cellulose crystal will become important. Fortunately, at that time, the application method will itself help sort through the various spectroscopic methods. For the present purposes, the author recommends that people largely ignore this metric as it is hopelessly unreliable as currently practiced. For purposes ofthe remainder of this chapter, the name CNCs will be used exclusively when the discussion is focused on the standard processing method using acid to hydrolyze the amorphous cellulose. The term cellulose nanorods (CNRs) will be used when the discussion is more general and refers to any of the methods used to generate rod-shaped particles. This is not to suggest that the concentrated acid method is more selective for crystallinity than other methods; given the current state of the art, this is not known. Rather, the acid methods have been intimately associated with cellulose crystals since the discovery by Ranby [9]. As an example, Segal et al. used acid hydrolysis crystallinity and leveling-off degree of polymerization (DP) as a standard method in developing the well-known Segal method for estimating crystallinity from wide angle X-ray scattering (WAXS) data [23]. The reference to crystallinity and use of the acronym CNC is simply a convenience.

23.1.3 Cellulose Nanocrystals (Cellulose Nanorods)

The material we refer to today as CNCs was first isolated by Ranby in 1949 [9]. The experiments were an effort to confirm the size of the crystals previously determined by X-ray diffraction and that the crystals were the residual cellulose after acid hydrolysis [24, 25]. Hydrolysis is the reverse of the cellulose synthase processi A molecule of water is inserted into the acetal bond to break the polymer chain between two glucose monomers. The reaction is often catalyzed with acids, where the proton attaches to the acetal oxygen that joins two monomers and initiates the bond cleavage. An OH’ is picked up from the surrounding water to stabilize the other end group, regenerating a proton in the process.

Ranby used dilute acid hydrolysis, isolated the subrnicron-sized particles that resulted, and characterized them using transmission electron microscopy, X-ray diffraction, and DP [9, 26]. This isolation method works because the rate of acid hydrolysis of the crystals is slower than the rate of hydrolysis of the amorphous

material [24, 26, 27]. The difference in rates appears to be due to a somewhat surprising feature of the cellulose crystal. When cellulose is placed in deuterium oxide, the deuterium atoms rapidly exchange with the native hydrogen atoms of cellulose in the amorphous portions of the fiber but the deuterium exchange inside the crystalline regions is very slow [28]. This suggests that acids (protons) penetrate the amorphous regions and hydrolysis occurs at a similar rate within the solid as at the surface. But the crystalline regions of the cellulose resist penetration by the acid and hydrolyze heterogeneously from the surface. This chemical resistance of the crystal is not just limited to acid hydrolysis. It also appears to work with oxidative degradation [29], biological degradation of cellulose [30], and other dilute and concentrated acids [31—33]. All of these methods can produce CNC-like rod-shaped particles, show at least some reactive preference for the amorphous regions of the cellulose, and provide a product that is more crystalline relative to the starting cellulose source.

The modern method for producing CNCs is not based on the Nickerson/Ranby method using 2.5 N sulfuric acid but rather on a method developed by Mukherjee and Woods several years later [34]. They were attempting to follow the course of acid hydrolysis using X-ray scattering. Acid concentrations of 550 gl -1 (~42%) and 900gl'l (~60%) had little impact on the crystal structure as determined by X-ray diffraction. When they increased the concentration above 900gl'l, they were no longer able to evaluate the cellulose fibers because they disintegrated into suspended nanoparticles when they were washed. They determined that CNCs could be readily isolated using acid strengths between 900 and 975 g l'l (~63%), but at 985 g1" (~64%) all the cellulose was hydrolyzed and when the reaction was stopped at short enough a time to recover cellulose, some had been converted to cellulose ll. The primary advantage of this method was the stronger acid reacted with the surface OH groups of the cellulose crystals, attaching sulfuric acid halfester groups. This causes the crystals to separate and disperse once the pH rises high enough for the protons to dissociate. A treatment with sulfuric acid at 955 gl-1 (62.5%), 40 °C, and 24 h was established by Marchessault in 1961 et al. [35]. Dong et al. partially optimized CNC preparation in 1998 based on the ordered phase separation and particle size [36]. More recently, Beck-Candanedo et al. [37] and Bondeson et al. [38] have optimized the preparation of CNCs, using slightly different parameters. Wang er al. offered optimizations based on total biomass utilization and a kinetic evaluation of the strong acid hydrolysis [39, 40]. Since the crystallinity of cellulose is thought to be one of the main barriers to enzyme saccharification of cellulose for biorefinery, research groups have also developed methods to isolate rod-shaped particles from biorefinery-based treatments [41].

23.2 Scale-Up and Production of Cellulose Nanocrystals

23.2.1 Process Scale and Processing Basics

At present, there are at least three pilot plants producing CNCs in North America using the 64% sulfuric acid method. CelluForce located in Windsor, Quebec,

is a joint venture between FPInnovations and Domtar. This plant is capable of producing about 1 mt per day of CNC. Relatively little has been published on this plant, but it appears to be a batch process using membrane filtration for final salt/acid removal. The CelluForce plant includes acid recovery and spray drying capability for producing a dry powder form. Alberta lnnovates Technology Futures has a smaller pilot plant in Edmonton, Alberta, capable of producing CNCs at the rate of 100 kg per week. Basic equipment in the plant includes two glass-lined reactors, a centrifuge for separation of the crude CNC and sulfuric acid, and a membrane filtration system for final acid/salt removal and concentration of the CNC product. Alberta lnnovates also has spray drying capability for producing a dry powder product. The US Forest Service established a pilot plant at the Forest Products Laboratory (FPL) in Madison, WI, for production of both CNCs [42] and the TEMPO grade of CNFs [43]. Production capability for CNC is 25 kg per batch and about 75 kg per week. The FPL facility includes freeze-drying capability but only for a small portion ofthe production. The FPL plant consists of a 4001 primary reactor for production of the CNC and two larger dilution tanks (4000 and 6000 l) for dilution and neutralization. All tanks are glass-lined steel. A membrane system is used for diafiltration and final concentration of the CNC suspensions. The FPL process does not include a centrifuge and does not attempt to recover acid or glucose.

All of these processes operate as batch processes using a scale-up of the laboratory procedures [37, 38]. The major change from laboratory methods is to use a membrane filter for acid/salt removal and final suspension concentration. This replaces the use of dialysis for the salt and glucose removal. The Alberta Innovates and FPL pilot facilities have taken slightly different approaches to several of the processing constraints for CNC, and the outcomes are instructive for future plant design. FPL based the plant on loading the reactor with shredded pulp and adding acid to the pulp; Alberta lnnovates has taken the opposite approach, adding shredded pulp to the stirred solution of acid. Both installations have had to address several addition and mixing-related problems with the reaction: charring at the acid-wetted surface, and gel formation of pulp that contacts the sulfuric acid but is not fully mixed into the pulp suspension. Charring can be avoided by making sure the cellulose is drawn into the acid fairly quickly, or exchanging air at the top of the reactor for nitrogen or another inert gas. Gel formation happens when a clump of cellulose contacts the acid, initiating hydrolysis and possibly dissolution of amorphous cellulose. But the entire mass of the cellulose particle does not get pulled into the acid solution and dispersed as individual fibers in the acid. It appears that this is a dissolution re-precipitation process where the re-precipitated cellulose creates an acid impenetrable layer that is too thick to hydrolyze during the typical 45-90 min retention time of the standard reaction. The Alberta lnnovates approach solves the mixing problem with better initial mixing that draws the cellulose into the acid solution and disperses it quickly. It however encounters a problem in operating at higher initial solids loading, resulting in a need for more acid relative to the CNC produced. FPL uses several sprayers mounted on the top of the reactor [42]. They displace the air in the reactor by pumping a vacuum on the vessel and refilling with nitrogen, and then force 64% sulfuric acid through the spray nozzles to saturate all the shredded pulp

in the reactor. This process is not able to start agitation until over half the acid has been added. As long as the initial spray distribution is adequate, the method works well and allows a higher initial solids loading, currently running at about 11% starting consistency [42]. The two installations took different approaches to the membrane filtration problems as well. The FPL installed larger diameter membrane tubes, which only provide about 0.1 ml of surface area per kilogram of product (batch). Diafiltration requires about 24 h. But the larger tubes handle higher viscosity suspensions, and the membrane system dewaters to about 13% solids for shipping and storage. Alberta Innovates installed a membrane system with much smaller tube diameters and much higher surface area per kilogram of product. They can complete the diafiltration in about 6 h, but can only dewater to about 4% solids before the viscosity is too high to pump the suspension through the tubes. Both of these compromises have costly consequences and a larger scale facility needs to plan on separating and optimizing the diafiltration and dewatering unit operations. Both Alberta Innovates and FPL are fully functional successful installations for the current task at hand, making CNC more readily available for product development.

Scale-up from the nominal 100 kg per week size to 1000 kg per day does not require substantial changes in process approach, but the 7000-90001 of waste acid becomes a much larger management problem. CelluForce presumably could have sent the once-used acid to the adjacent Domtar mill, but chose instead to initiate work on acid recovery [44]. Effective acid recovery will almost certainly be required of plants significantly larger than the CelluForce facility. The recovered acid contains about 5% (by weight) glucose, caramelized acid degradation products, and trace metals from the starting pulp, chemicals, and corrosion of process equipment. It is not suitable for all applications in a mill.

There are, in addition, several pilot plants utilizing alternative chemistries to isolate a rod-shaped cellulose nanoparticle [45]. In particular,

- Bluegoose Biorefinery (30 kg per week, Saskatoon, SK), which appears to use a Penton radical approach;
- American Process Inc. (1 mt per day, Thomaston, GA), which uses an acid sulfite approach.

The major decision in building a larger scale plant is whether the facility will operate with batch processing or a continuous system. Batch processing does not present significant problems at smaller scales, but as the scale increases, the time to load and discharge the hydrolysis reactor and to dilute and process the crude CNC will begin to affect the uniformity and yield of the CNC product. Batch processing requires excellent mixing at the early stages of the hydrolysis reaction and this is diflicult to accomplish with high pulp solids when working in large tanks. Standard agitators on shaft mixers do not mix 10% consistency wood pulp effectively and this application will require other designs. Although batch processes in the range of 10 mt per day may make economic sense, scale-up much beyond 10 mt will probably benefit by a switch to a continuous process. Even at the 10 mt per day scale, dilution, separation, neutralization, diafiltration, and concentration may all switch to continuous processes since the required tank volumes will get much larger and the membrane processes require the same surface

area per daily ton, regardless of use in a batch/recycle or series-continuous operation. Generally, a continuous process can provide better manufacturing control and reduce the labor needed to control and maintain the process.

The selection of batch or continuous process can be affected by, or otherwise influence, the choice of materials of construction. The viability of glass-lined mild steel reactors decreases with increasing size, 91 0001 being the largest offered by one ofthe manufacturers. At that scale (12 mt of pulp per batch) the time required to load and discharge the reactor becomes significant, and the shaft mixer normally supplied with glass-lined equipment is ineffective. A switch to continuous processes eliminates the mixing problem, but lined pipes and reactors have a poor track record in continuous processes where there is more abrasion and erosion. Standard austenitic stainless steels 316 and 317 are not suitable for use with 64% sulfuric acid [46]. The alloy 20 type stainless steels (Carpenter 20, Duramet Alloy 20, ACI CN-7M) have corrosion rates below 0.13 mm per year in 64% sulfuric acid and temperatures below 50°C. These alloys are less suitable at higher temperatures in non-oxidizing or air-free conditions and this is a concern since the reaction space around the CNC process conditions does not appear to have been evaluated in detail. Nickel-based alloys including lncoloy and Hastelloy appear to provide similar resistance to sulfuric acid corrosion. Corrosion resistance for stainless steel and several more suitable alloys is shown in Table 23.1. Methods for producing CNRs using acids other than sulfuric acid or alternative chemistries have different and, in some cases, more serious and costly corrosion issues.

In producing CNRs, a company needs to address the question of where the facility is to be located. The product is either a dilute suspension in water or a low-density powder. It is not generally desirable to ship either water or air. They add considerable cost to the delivery of a product and provide a huge cost advantage to local producers. The solution for products incorporating cellulose nanomaterials is to produce the CNR near the product site by either locating production near a pulp mill/CNR plant or building a CNR production facility near the plant that will produce the final or intermediate product. With production of CNC, there is little manufacturing advantage in locating next to a pulp mill. The primary value of starting with never dried pulp is to avoid the cost of drying the sheet. But because the CNC process requires high concentration sulfuric acid, never dried pulp complicates the process of charging and mixing:

- Assuming the pulp is pressed to about 45% solids for the CNC plant, the sulfuric acid concentration needs to be raised to about 74% solids to compensate. Mixing then becomes even more critical because insufficient mixing will leave some pulp in sulfuric acid at high enough concentration to dissolve the cellulose [48]. Mukherjee claimed the yield of crystals dropped off substantially at 985gl-1 (about 64%) [34] and Wang et al. showed that the yield of CNC was substantially reduced at 66% sulfuric acid [39].

- The exotherm from dilution of the 74% sulfuric acid to 64% will raise the process temperature to about 25 °C. This could add a requirement for cooling the sulfuric acid or the reactor. The target process temperature of45 “C becomes a problem in regions where the storage temperature of the acid rises above 20 “C during warmer months.

Table 23.1 Alloy corrosion by sulfuric acid [47].

Common name	AISI alloy name	UNS designation	Temperature (°C)	% Sulfuric acid	Rate (mm yr^{-1}) (N_2)	Rate (mm yr^{-1}) (air)	Cost factor
Carbon steel			50	64	1.5	—	1
316	316	S31600	50	35	21	1.6	1.7
				64	40	5	
904L	904L	NO8904	50	35	<0.11	—	9.7
				64	<0.11	—	
Carpenter alloy 20	20 Cb-3	N08020	50	35	<0.1	—	6
				64	0.1	—	
Incoloy 825	825	N08825	50	35	0.2	—	9.7
				64	0.13	—	
Hastelloy G	G	N06007	50	35	<0.13	—	11
				64	<0.13	—	
Hastelloy C-276	C-276	N10276	50	35	<0.13	—	11
				64	0.13	—	
Monel 400	400	N04400	60	35	0.2	1.5	9.5
				64	0.25	1.0	

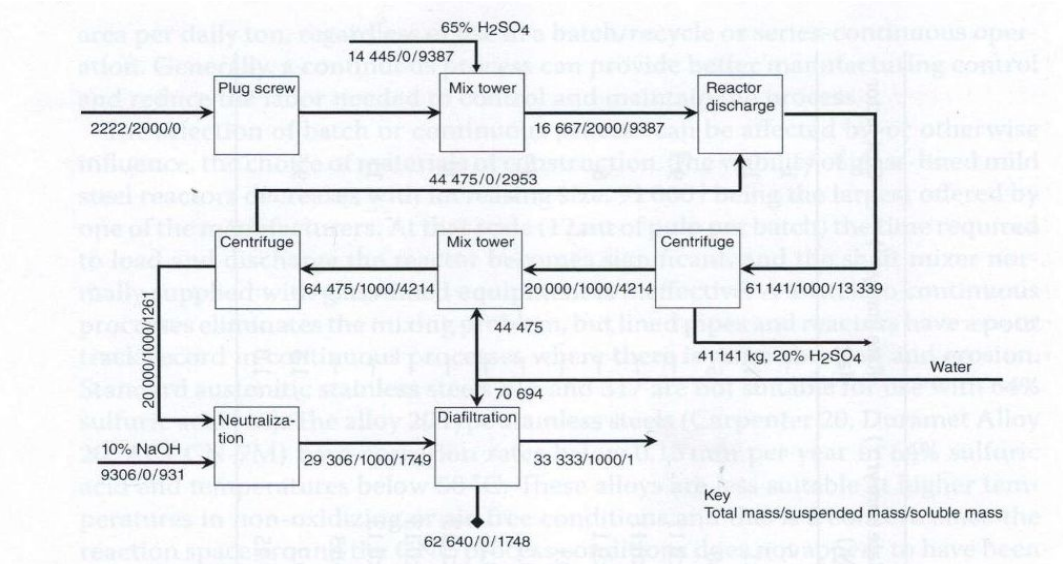


Figure 23.1 Block diagram and mass balance for a CNC plant.

- There are reports that the fraction of cellulose in the crystalline state increases on drying [49].

Without data on yield of CNC for dried and never dried pulps, the possible economic advantages for co-locating CNC and applications plants next to a pulp mill are speculative, but with current information, constructing a plant to run on market pulp and adjacent to existing plasticsl composites manufacturing facilities appears to be preferable. A second factor to be considered in location is the use of spent sulfuric acid. The cost of the sulfuric acid needed to produce CNC is four to six times larger than the cost of the market pulp (Table 23.3, vide infra). Assuming some expense to recover and reuse sulfuric acid, locating near a facility that can use the spent sulfuric acid can provide a considerable cost advantage.

A proposed block schematic and mass balance for a CNC production facility is shown in Figure 23.1. The major unit operations include pulp handling, feeding pulp to the reactor, mixing, retention time, discharge, dilution, crude CNC separation, neutralization, CNC purification, CNC concentration, CNC drying, and acid recovery. With the exception of acid recovery, all of these unit opera» tions are standard processes in pulp mills or chemical plants. The block diagram assumes the use ofcentrifuges to separate the crude CNC from sulfuric acid, and collection of sulfuric acid at 20% for concentration and reuse.

23.2.2 Feeding Pulp to the Reaction System and Mixing with Sulfuric Acid

The paper industry has two processes used for feeding and mixing pulps at high consistencies. In mechanical pulping, peroxide bleaching is carried out at about 20% solids by mixing pulp at 30-40% solids with the peroxide bleaching solution. Shredded pulp is fed to an auger, which in turn feeds the pulp to the eye of a horizontally mounted disk refiner. The sulfuric acid solution would also be

pumped to the center of the disks and would become intimately blended with the pulp as both progress through the rotating disks. When used for fluthng pulp or mixing peroxide in high-consistency mechanical pulp, the refiner sucks in a lot of air, which is then used like a blower to convey the pulp to the top of a storage tower. This air will present a problem for production of CNC and may require the process to blanket the inlet with nitrogen or another inert gas. Potential concerns about this type of process are that the mixing occurs over a very short time and that the shredded pulp sheets might not disperse into individual fibers within the refiner/mixer. Also, it is difficult to maintain a smooth flow of shredded pulp to a mixer and the short retention time does not provide for any time~blending of materials. In addition, the rotating element is under considerable g~forces and providing materials of construction suitable for sulfuric acid service, and the rotational g-forces of the mixer might add to the costs.

The second possibility is equipment in high yield pulp mills designed to assist chemical penetration into wood chips. In this system, wood chips are pressed to produce an impermeable plug and the plug forced into a flooded reactor zone. The chips expand when released from the plug and are dispersed by a vertical auger into the added chemical solution. Typically, chips are conveyed above the solution level by the auger. This allows excess chemical solution to drain from the chips, which then spill over the top of the chemical mixing system into a retention vessel. A plant schematic for this type of system is shown in Figure 23.2. For CNC production, shredded machine dried pulp would be fed to the plug screw feeder and the plug forced into the sulfuric acid solution at the bottom of the chemical mixing zone. Instead of a vertical auger to convey material to the top of the mix reactor, a peg mixer could be substituted and the force necessary to convey the pulp to the top of the mixer apparatus supplied by the sulfuric acid and pulp feeds. Potential advantages of this method are that the plug forming reduces air in the reaction, and by forcing pulp into the bottom of a flooded reactor, there is no surface reaction where charring could take place. The reactor mixing zone

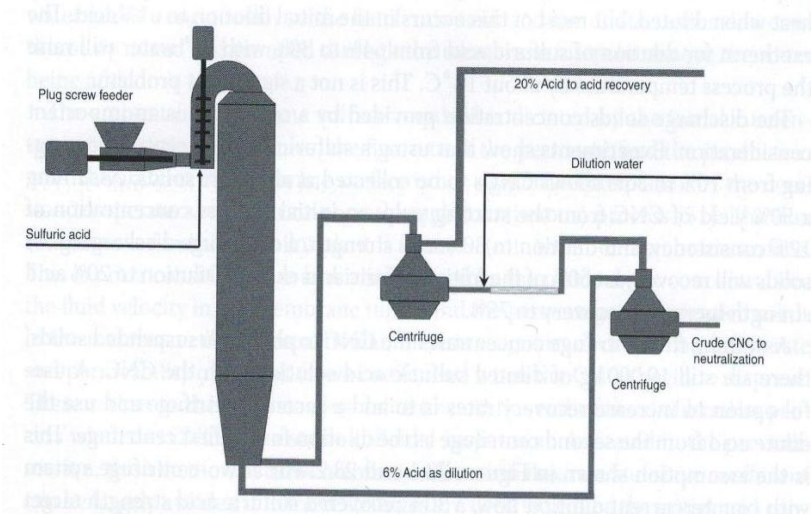


Figure 23.2 Schematic for a plug screw feeder-based CNC hydrolysis plant.

provides enough retention time to blend out flow variations in the pulp and is still small enough to supply significant mixing intensity without excessive power.

Once pulp and sulfuric acid have been mixed sufficiently that the pulp is dispersed into individual fibers, there is little need for further mixing and the remainder ofthe reactor is just a retention tower with a suitable outlet mixer and valve. Since the reaction temperature is low and the reaction is at atmospheric pressure, there is little demand on the materials of construction beyond the considerable need for resistance to sulfuric acid. Both polyvinyl chloride (PVC) and polyethylene are suitable for these conditions.

After maintaining the suspension conditions for the required reaction period, stopping the hydrolysis reaction and recovering concentrated sulfuric acid are required. Filters and centrifuges are generally used in chemical process industries to remove a solid from suspension. Filtration can be difficult with cellulose nanomaterials because the small particles form highly impervious filter cakes. Filtration can be improved by adding water~miscible solvents or other chemical filter»aids, but these all add another contaminant that needs to be removed, and in the case of solvents, recovered.

23.2.3 Product Separation Using Centrifuges

Use of a centrifuge also requires process adjustments. Sulfuric acid at 64% strength has a viscosity of 5 mPas and a density of 1.52gcm-3. The density is very close to the density of cellulose crystals (1.58 gcm-3 for the la form, and 1.6gcm'3 for the Ifi form [50]) and the solution viscosity further complicates separation of CNCs. Dilution to 35% acid strength reduces the viscosity to 1.2 mPas and the density to 1.25gcm-3, sufficient to collect the CNC using a centrifuge. This will likely be required for acid recovery using centrifuges. As a process adjustment, it adds an initial dilution step to processing, either at the bottom or discharge of the reaction tower, or in the pipe delivering the acid suspension to the centrifuge. Concentrated sulfuric acid gives off considerable heat when diluted, but most of this occurs in the initial dilution to 64% acid. The exotherm for dilution of sulfuric acid from 64% to 30% with 25° water will raise the process temperature by about 10 “C. This is not a significant problem.

The discharge solids concentration provided by a centrifuge is an important consideration. Experiments show that using a sulfuric acid concentration rang» ing from 10% to 30% allows CNCs to be collected at about 5% solids. Assuming a 50% yield of CNC from the starting pulp, an initial process concentration of 12% consistency, and dilution to 30% acid strength, a centrifuge discharging 5% solids will recoverjust 60% ofthe initial sulfuric acid charge. Dilution to 20% acid strength increases recovery to 75%.

Assuming the centrifuge concentrates the CNC to about 5% suspended solids, there are still 19 000 kg of diluted sulfuric acid solution with the CNC. A useful option to increase recovery rates is to add a second centrifuge and use the dilute acid from the second centrifuge as the dilution for the first centrifuge. This is the assumption shown in Figures 23.1 and 23.2. For a two-centrifuge system with countercurrent dilution flow, a 30% recovered sulfuric acid strength target requires the second stage to be diluted to 12.5% sulfuric acid concentration and

recovers 75% of the sulfuric acid used in the process. To recover 20% acid, the spent acid to the second stage centrifuge needs to be diluted to 6% sulfuric acid and the total recovery rises to 88%. Using reasonable assumptions for steam, sulfuric acid, and neutralization costs, recovering sulfuric acid at 20% concentration is cost effective (Figure 23.1).

Use of a third stage centrifuge with dilution to 1% acid or less reduces the salt concentration after neutralization sufficiently to avoid a flux-rate bottleneck in diafiltration (vide infra). This third centrifuge could also be integrated into the countercurrent dilution scheme to further increase the acid recovery rate. It is expected, however, that the process will need to discharge some sulfuric acid. In addition to glucose, cellulose oligomers, and some degradation products, the acid will collect any trace metals in the starting pulp and any metals released into the process from corrosion and erosion. It will be very difficult to remove trace metals in acid recovery, and purging a portion of the sulfuric acid should be considered to control this accumulation. An alternative use ofthe filtrate from a third stage centrifuge might be to collect the dilute acid stream for neutralization with lime. This option reduces the amount of sodium hydroxide or sodium carbonate needed to neutralize the final CNC suspension for diafiltration and also reduces the salt concentration in the process effluent.

23.2.4 Product Purification, Diafiltration

After separation, a CNC plant will either go direct to diafiltration or neutral» ization followed by diafiltration. Neutralized suspensions are more stable both physically and chemically, but some applications may be better served by CNC isolated in the acid form. Neutralization also simplifies the choice of equipment metallurgy and filter media for the membrane filtration plant. Diafiltration is simply dilution followed by a filtration concentrating process. This is repeated several times, ultimately requiring 6—10 times more process water than the amount contained in the crude product. Most systems operate in a batch mode with dilution water added continuously to the batch mix tank and the dilute suspension con» tinuously mixed and pumped through the membrane filters to remove the water being added.

The amount of membrane surface required is dictated by the initial concentration fed to the membranes, the flux rate of the permeate, and the production rate. The amount of membrane surface is not significantly impacted by the deci» sion to operate as a batch or once through (continuous) process [51]. The flux rate observed in the FPL pilot plant is about 61 (min m2)-1 of membrane surface. This is not a constant value and is influenced by the residual salt concentration, the fluid velocity in the membrane tubes, and the percentage of suspended solids in the membrane tubes. In particular, there is a significant drop in both flux rate and permeability of the salt (sieve coefficient) when the CNCs begin to disperse. These return to the near-starting value toward the end of the diafiltration pro» cess when the CNCs are a stable colloidal suspension. As stated in the previous section, this situation ofa low membrane filtration flux rate and sieve coeflicient can be largely avoided if extra centrifuges are used to reduce the initial acid con» centration to about 1% before neutralizing.

Table 23.2 Estimated diafiltration efficiency relative to discharge solids concentration and with or without countercurrent filtrate recycle.

Discharge % solids	3%		6%		10%	
Water recycle	No	Yes	No	Yes	No	Yes
Stages required	8	9	5	5	4	4
Water use (m^3 mt^{-1})	480	80	417	83	360	90
Na_2SO_4 in filtrate (%)	0.51	3.1	0.59	2.9	0.68	2.7

Simulation goal is less than 1 kg Na_2SO_4 per metric ton of CNC product. Input is 7.5% sodium sulfate.

The viscosity of the CNC suspension begins to rise significantly above 3% solids, and this is about the limit for small tube membrane systems. Assuming dilution to 1% between stages and dewatering to 3% in each stage, a plant producing 100 mt per day of CNC will require about 7000 m2 per stage~equivalent of diafiltration and will require about eight stages to reduce the sodium sulfate concentration to below 1 kg mt" of product. This analysis is based on an initial sodium sulfate concentration of 7.5%, similar to what can be obtained using a two~centrifuge acid recovery process.

The summary provided in Table 23.2 shows how the number of stages and water requirements are impacted by membrane discharge consistency. With the assumption of a 1% inlet consistency and 3% discharge consistency, the same level of purification can be achieved using a countercurrent filtrate process but will require an additional stage of membrane filters. Countercurrent use of permeate will also reduce the water use in diafiltration from 480 to 67-80 m3 mt'l. The process water used in the diafiltration has to be deionized to avoid contaminating the product with multivalent metal ions. The significant reduction in water use with a countercurrent filtrate system can provide considerable capital savings in a much smaller deionizer or reverse osmosis (RO) system. While the use of countercurrent filtrate flow requires a 30% increase in membrane surface area for filtration, it reduces the RO system requirements by 85%. With single use water flow in diafiltration, the combined process filtrate contains just over 0.5% dissolved sodium sulfate, but with countercurrent use of filtrates, the discharge concentration of sodium sulfate rises to 3%. Salts are expensive to remove from a wastewater stream and this concentration is too high to discharge directly into a low-flow receiving stream. The use of lime to neutralize waste acid and precipitate calcium sulfate may be necessary to operate in arid regions.

The eificiency of diafiltration is heavily dependent on the discharge consistency. The membrane filtration system can dewater to >10% solids, but requires higher flow velocity to utilize the shear thinning properties of the CNC, and a membrane system that can handle the viscous suspension without plugging. The shear thinning properties of the CNC vary with ionic strength and maintaining fluid conditions would likely require adding dispersants until the salt concentration is low enough to provide more stable suspensions. However, raising the discharge solids to 10% theoretically enables purification to l kg ofsodium sulfate per mt of

CNCs in just four stages of diafiltration. An added concern is that CNC suspensions do not behave in an ideal manner and flux rates slow down considerably at higher suspension solids. These problems all need to be resolved to achieve the volumes and efficiencies suggested in Table 23.2 since the analysis is based on ideal behaviors.

23.2.5 Product Drying

The existing pilot plants use either spray drying or freeze-drying (lyophilizing) to produce a dry product. Neither is particularly suitable for scale-up. It is hard to envision increasing the scale of a freeze-drying process to produce several metric tons per day of the dry CNC product. The process is very slow and requires several days of vacuum drying even with a very well-designed system. It is not considered to be commercially viable at the multitons per day scale and the ability to redisperse the dried powder is marginal [52]. Although more scalable, spray drying is not a major improvement. First, the dry product is hydrogen-bonded aggregates of CNC that are very difficult to redisperse to the individualized particle state. Beck et al. show a 1 G] mt-1 sonic energy requirement to return the CNC to the original never dried average particle size [52]. Heat requirements for drying are also quite large, over 25 000 M] mt-1. However, it appears to be the only current system capable of scale-up as needed.

There have been multiple investigations of solvent drying methods on cotton, wood, and wood pulps, and these possibilities need to be considered. In an extensive study of drying methods, Merchant showed that the results of freeze-drying were dependent on the temperature, and the maximum wood pulp fiber surface area 0f3.2 m2 g‘1 was achieved when maintaining the fibers at -195 °C [53]. This compares to a surface area of about 1 m2 g-1 for pulp dried from water [54]. Solvent drying using methanol followed by pentane provided a surface area of 133 m2 g-1 [53].

With CNCs, solvent exchange methods can have a difficult time maintaining the CNC suspension during the transition to a nonaqueous and nonprotic medium. Once water is completely removed, however, the collapse of the suspension should not result in significant hydrogen bonding between crystals on final solvent removal. Solvent exchange from water will require a membrane filtration system to remove the water/ solvent mixture [55, 56]. Once the suspension collapses, the crystals can be isolated using a centrifuge and the remainder of the solvent exchange process carried out at higher solids concentrations and with less solvent volume. One version of solvent exchange drying is referred to as critical point drying; the final solvent evaporation is carried out above the critical point of the final solvent. This method minimizes coalescence of material due to the residual surface tension of the final solvent. The process is often accomplished with a third solvent exchange, from hydrocarbons to carbon dioxide, as it is easier to manage at the critical point and works well. A comparison of wood pulp dried directly from water, by solvent exchange and by critical point drying shows an increase in surface area from 0.4 mg2 g-1 after direct drying, to 43 ml g" after solvent exchange and further increase to 144 m2 g-1 with critical point drying using CO2 [57].

Yet another approach to solvent exchange is to start with a high boiling solvent. Using r1-butanol, the azeotrope contains as much as 44% water, greatly reducing the amount of alcohol required in the first exchange stage [58, 59]. Since the n-butanol boils at 117°, the residual water content is very low as butanol continues to be boiled off of the CNC suspension. Solvent exchange to pentane or CO2 can then be used to reduce the surface tension and the amount of hydrogen bonding in the dried CNC. A similar approach can be taken with high boiling non-azeotropic solvents, with dimethylsulfoxide (DMSO) or dimethylformamide (DMF) as examples. These have been used quite successfully at laboratory scale to transition cellulose nanoparticles into a nonaqueous system and disperse them in solvent-soluble polymers [60, 61]. Evaporation of these solvents is troublesome, but solvent exchange from DMF as example to pentane should be relatively straightforward and the results similar to the more familiar solvent exchange processes. While this can significantly reduce the amount of first exchange solvent needed, it does raise a problem with recovery and recycle ofthe first exchange solvent. Since the water would be evaporated (distilled) away from DMF (or DMSO), the resulting still bottoms also contain anything collected in the system that is not volatile. Continued reuse of the high boiling solvent without distillation or other purification steps is not viable.

Solvent exchange is energy intensive and will likely be of higher operating cost than spray drying. Although density, boiling point, and enthalpy of vaporization are all considerably lower for methanol and pentane than water, the 10 to 1 volume expansion needed for solvent exchange adds a considerable distillation volume and thermal load. Use of the n-butanol azeotrope will reduce the first solvent to about 1.5 times the amount of water in the suspension, but has the added problem of removing the water from butanol in order to recycle the solvent. \X/hen using high boiling solvents such as DMP or DMSO, the water is distilled away from the solvent, they require at least one additional solvent exchange in order to transition the CNC to a near-dry state, and require some sort of cleanup process for the high boiling solvent. A possible advantage with high boiling solvents is the ability to use multiple effect evaporators to remove the water from the initial suspension but all of these options should have a considerably greater thermal load than spray drying. In an integrated process, they have an advantage because ofthe ability to use waste or low value heat. Ultimately, product processing needs are likely to dictate drying methods. Assuming the solvent methods can provide a more readily dispersed CNC product, this may be necessary to effectively disperse the CNC in resins for composite products.

23.2.6 Acid Recovery

Acid is the largest cost item in CNC production and without an effective recovery option, direct variable costs will increase by a factor of 2—3 (Table 23.3). Nothing else is close to the sulfuric acid cost and recovery has to be regarded as the number one critical need to control production costs for CNC. Unfortunately, this is not a new problem and has resisted effective solution for a century or more. The very first concepts for production of sugars from biomass utilized concentrated acids. These processes never succeeded commercially because they needed effective

Table 23.3 Cost items in production ofCNC.

Item	Name	Amount (kg)	Low (cost) value ($)	High (cost) value ($)
Product and co-products				
	CNC product	1 000	5 000	10 000
	Value of glucose	1 000	100	250
Major cost items				
	Pulp	2 000	500	1 500
	Sulfuric acid (no recovery)	16 500	3 000	5 000
	Acid makeup (with recovery)	1 759	300	550
	Caustic	730	300	450

All values are estimates.

acid recovery to be profitable, In 2007, the US Department of Energy awarded a $40 million grant to BlueFire Ethanol to build a 19 million gallon per year ethanol plant using a concentrated acid biomass hydrolysis process with acid recovery. Although BlueFire Ethanol (Now BlueFire Renewables) still exists, 8 years later, it is still trying to build that initial plant. There are a number of acid collection and recycle systems under consideration [44, 62, 63], but to date none seems to be working well and ready for a large-scale production need.

The problems in recovering both sugars and sulfuric acid at a concentration high enough to economically reconcentrate the sulfuric acid to 70% or more are daunting. For a CNC plant, there is an easy way out and that is to not recover the sugar in the waste acid, and focus on reducing the overall expense and energy intensity ofthe process byjust recovering the acid. This is a much more tractable engineering problem but does sacrifice the $100-250 (per metric ton of CNC) of glucose by-product. The cost difference between no recovery and 93% acid recovery is in the range of $2500—450O mt-1 of CNC. Sacrificing the $200 value of the glucose is cost effective if adding equipment for the sugar separation compromises sulfuric acid recovery. Note the costs listed in Table 23.3 do not include the cost ofevaporation and other steps required to recover acid or the cost of neu» tralizing all the acid rather than just the estimated 7-11% that is not recovered.

The following are the proposed process steps:

1) Separate the CNC product from the acid at as high an acid concentration as possible.
2) Wet-air combust the sugars and other organic materials in the acid stream by raising the process temperature and adding oxygen [64].
3) Clean up the acid; it may require filtration or centrifugation and treatment with activated charcoal to remove trace contaminants.
4) Reconcentrate the sulfuric acid from approximately 20% concentration to approximately 70% concentration for reuse.

23.2.7 Scale-Up and Production Status of Cellulose Nanocrystals

At present, there are at least three pilot plants producing traditional sulfuric acid hydrolysis CNC in North America. CelluForce, the joint venture between Domtar and FPInnovations, is the largest at nominally 1 mt per day. CelluForce is the only organization with installed and tested acid recovery but there is no published information on the efficiency or cost of the process. CelluForce has also initiated planning for the next larger size plant. Unfortunately, they are the most secretive of the three pilot facilities and are very focused on intellectual property management with their partners. Very little public information is available on the plant or process. The US Forest Service pilot plant at the FPL is the smallest of the three but has made CNC available for general purchase through an arrangement with the University of Maine Process Development Center. Alberta Innovates Technology Futures is the most recent of the three to come on line. Slightly larger than the FPL facility, they have considerable flexibility with equipment and process. All three pilot plants are batch operations. The biggest message from three successful pilot plants is that this is not an impossible engineering problem and construction of a larger scale semicommercial or commercial plant is not beyond more or less routine engineering requirements. Critical information needs are improved data on drying methods and a validated acid recovery process. Drying methods should include solvent exchange and critical point drying. If a wet air oxidation process is considered for acid recovery, information on oxidation efficiency of glucose in 20-30% sulfuric acid, and ancillary clean-up are needed.

23.3 Cellulose Nanofibrils

23.3.1 The Different Methods and Forms

CNPs are a broad group of cellulose-derived micron and nanoscale filamentous particles. Each of the processes produces generally similar particle morphologies. The average particle diameter and length are usually dependent on the amount of energy invested in the “disintegration” process. The initial concept of CNF is really glassine papers that were produced by beating pulps to the point that drainage was quite slow, but bonding between fibers, fibrils, and fines was extensive enough to reduce scattering and provide a translucent to transparent sheet. The first real fibrils, refined beyond glassine, were produced at Rayonier Corporation using multiple passes through a homogenizer. The process disintegrated the wood fiber cell walls and provided a very high surface area fibrillar product [65]. ln the last decade, similar materials have been produced using low-consistency refiners operating in series [66], a horizontal grinder using specialized ceramic stones [67, 68], and both impinging flow [69, 70] and opposed valve homogenizers [65]. The principal breakthroughs were provided when scientists discovered that oxidative [71], acid [70], or enzymatic pretreatments [69] significantly reduced the energy required to produce nanoscale fibrils from native cellulose. Direct mechanical reduction of wood pulp to CNF is reported

to require 20-30 MWh mt^{-1} in refiner and/or homogenizer specific energy. The enzyme pretreatment process reduces this to as low as 1 MWh mt^{-1} [72] and the TEMPO style pretreatment reduces it further to about 500 kWh mt^{-1}.

Each of these product types and production methods requires a different production process, has different scale-up barriers, and is at different stages in the scale-up path between laboratory and commercial scale. The farthest along is probably the treatment of wood pulp with a string of refiners to produce micro- and nanofibrillated products. Nakagaito and Yano showed in 2004 that conventional stock preparation refiners were able to provide many of the application benefits of CNF, but ultimately additional treatment with homogenizers was needed to maximize the strength obtained when using the fibrils in a composite [66]. Unfortunately, the refiner treatment required between 16 and 30 refiner passes to achieve benefits of a micron-scale or nanoscale fibrillated particle [66]. Pretreatments with dilute acid or enzymes can significantly reduce the number of refiner passes required and overall energy applied to achieve a nanoscale product. In contrast, most of the laboratory and small pilot-scale efforts have processed fibers with homogenizers. These devices have limited capacity, poor scale-up prospects, and are high maintenance under the very high pressures needed to produce CNF. They have been very useful and effective at the laboratory and pilot scale, but may not provide a useful method for multiton-scale plants. The use of the Masuko grinder and various extruder systems appears to be more promising in terms of a scalable process.

Various pilot plants have been assembled to produce this "grade" of CNF, including pilot facilities at VTT (Finland), Innventia (Sweden), the University of Maine (US), paper companies UPM Kymmene and Stora Enso (Finland/Sweden), Nippon Paper, Oji Paper, and DaiCel (Japan), Borregaard (Norway), and Kruger (Canada). These pilot plants appear to be working with all the mechanical methods identified: the University of Maine is using refiners, Innventia, homogenizers, and Oji the Masuko, grinder. Nippon and FPL are working with the TEMPO pretreatment method, and Innventia has worked with several pretreatment methods including both enzymes and carboxymethylation with chloroacetic acid among others. Borregaard, Kruger, and Nippon are of semicommercial scale at 5 or more mt per day. In addition, Imerys is producing a blended product of cellulose co-ground with traditional papermaking pigments and had one announced operating plant and at least one papermill customer. Unfortunately, the initial mill closed but the plant has been moved to another site and is in operation supporting another papermill. The Imerys process uses conventional mineral-grinding technologies.

A common characteristic of the CNF plants is that they are not significantly outside of the paper industry or other commercial industrial experience. Acid and enzyme treatments and stringing together a series of refiners are all common in the paper industry. The specific technology of refiner plate type and refiner operation are unique to the CNF product but can be identified by trial and error experimentation and consultation with refiner plate suppliers. Operation of homogenizers, extruders, and the Masuko grinder are not common in the paper industry but there are decades of industrial experience with these unit operations.

23.3.2 TEMPO and Related Pretreatments

The higher energy requirements of alternative methods and high performance properties of the TEMPO-pretreated CNF material have made this an active area of research and scale-up. In addition to two treatment methods with TEMPO, a chemical oxidation method with periodate [73] and a method of introducing carboxylic acids by modifying the industrial process to produce carbomethoxy cellulose [74] have been demonstrated. Cationized fibrils have also been prepared by reacting wood pulp with *N*-(2,3-epoxypropyl)trimethylammonium chloride [75], or adjusting the periodate oxidizing treatment to stop at aldehydes, which were converted to amines by reductive amination [29].
The TEMPO treatment and other chemical pretreatment methods that introduce ionic groups on the surface of the fibrils all have the same objective, to induce swelling. The swelling pressure facilitates disruption of the cell wall, which disintegrates into uniform fibrils at relatively low applied energy. While the TEMPO and periodate reactions are carried out in water and can start directly with wood pulps, the carboxymethyl cellulose procedure requires transferring the starting pulp into alcohol for the reaction and back into water for disintegration. Solvents and a solvent recovery process will add to the expense of the chloroacetic acid procedure.

23.3.3 TEMPO Oxidation of Primary Alcohols

The oxidation of alcohols with the free radical TEMPO was probably first identified by Golubev et al. [76]. The ability of TEMPO to selectively oxidize the C-6 carbon of glucose and polysaccharides was identified in various publications between 1992 and 1995 [77]. The difference in reaction efficiency for soluble, amorphous, and native forms of cellulose was noted by Isogai and Kato [78]. Saito and Isogai first reported the use of TEMPO oxidation to prepare string-like microfibrils of 3—5 nm diameter [71]. Saito et al. later added an alternative treatment using sodium chlorite as the primary oxidant [79]. This method does not provide as high a carboxylic acid functional group content as sodium hypochlorite (0.8 mmolg-1 vs 1.5 mmol g^{-1}) but the resulting fibrils are reported to be longer, have a higher DP, and form stronger films. The sodium chlorite reaction is considerably slower than that with the use of hypochlorite. The active primary oxidant is probably chlorous acid or chlorine dioxide generated in situ and these reactions are promoted by lower pH [80]. The lower final carboxylic acid content could be a result of reduced fiber swelling at the neutral pH. Hirota et al. have shown that 4-acetamido»TEMPO and sodium chlorite were effective at oxidizing the C-6 carbon of regenerated cellulose at pH4.8—6.8 [81]. This TEMPO analog has also been evaluated on bleached wood pulps at low pH, but with surprisingly different outcomes for hardwoods and softwoods. Using 4--acetamido-TEMPO to oxidize softwood pulp provided a carboxylic acid content of 1.2 meq g^{-1} at pH 6.7 and 1.3 meq g^{-1} at pH 4.8. When oxidizing hardwood pulp, the oxidation level dropped to 0.7 meq g^{-1}, similar to what has been routinely observed with the chlorite method when using the regular form of TEMPO [82].

Since the sodium hypochlorite reaction is more or less the standard approach, this reaction will be used as the basis for a discussion on scale-up for commercial scale production of the TEMPO grade of CNF.

Using typical reaction conditions [83], treatment of l mt of wood pulp requires 16.0kg TEMPO, 100 kg NaBr, and 1000001 of water. Sodium hypochlorite (375 kg) is added either all at once or over a period of time. During the reaction, sodium hydroxide is added as needed to maintain the pH at 10-10.5. For a final product with 1.5 meq g^{-1} carboxylic acid content, about 60 kg of sodium hydroxide is required.

As with CNCs, there are several trade-offs or compromises that inform selection of either a batch or continuous process. Batch process has the advantage of continuous pH adjustment and sodium hypochlorite addition, but the low reaction solids content requires large tanks relative to the amount of product produced. Very large tanks are difficult to mix and the time needed to achieve uniform mixing increases with size. Between 40 000 and 400 0001, mixing times become long enough that the batch system becomes impractical and further increases in scale would require multiple reactors. The level of turbulence at the mixer blade needs to increase with tank and agitator size, and at large enough volume, will initiate fiber disintegration. This needs to be avoided in order to wash the treated pulp and recover the TEMPO catalyst.

Once the process scale reaches a point where multiple batch reactors are needed, converting to a continuous process with mixing between retention stages has substantial advantages in labor and power. Because mixing volumes are smaller in a continuous process, mixing improves and maintaining plug flow through the process becomes the challenge to achieving process uniformity. As stated above, the TEMPO-treated fibers are shear sensitive near the end of the reaction and care is needed to avoid initial disintegration of the pulp. This is a concern for both batch and continuous processes. TEMPO-oxidized pulp looks and behaves like a bleached wood pulp. Drainage rate and water retention are not significantly changed relative to the starting pulp and it can be washed in conventional pulp washers or presses. Once the treated pulp begins to swell and form a gel, TEMPO recovery requires diafiltration and much larger volumes of water.

Several Research and Development (R&D) concerns have to be addressed for significant scale-up and engineering of a continuous process:

- A better understanding of the process kinetics to determine reactor sizes (retention time) and identify a control strategy.
- A check on process thermodynamics to assure that heating or cooling needs are met.
- A better understanding of how shear sensitivity develops through the treatment.
- An improved understanding of TEMPO recovery and reuse. TEMPO is an expensive chemical and is still largely active at the end of the reaction. Recovery and reuse are important to reducing production costs.

There is preliminary data available on each of these issues.

23.3.4 Kinetics

The kinetics of the TEMPO reaction have been addressed by several authors, including several papers on treatment of insoluble carbohydrates such as cellulose. Most of the kinetic work has been fit to a first order reaction based on available primary alcohol groups. The data in Figure 23.3 shows the production of carboxylic acid groups in thermomechanical pulp (TMP) over time and at three TEMPO charges. Mao et al. found that the kinetics fit a first order approximation [84-] and were similar to the TEMPO oxidation of rayon [85]. Unlike rayon, which dissolves during the reaction, the fraction of primary hydroxyl groups accessible to the TEMPO required an adjustment. As had been observed with rayon, the rate of oxidation for TMP had a linear dependence on the sodium bromide and TEMPO charges [85]. Both the first order rate and dependence on TEMPO, NaBr, and pH had been reported previously for TEMPO oxidations of glucan [77]. There are several limitations of the thermomechanical pulp kinetic data in Figure 23.3 that caution against generalization. Thermomechanical pulp has a composition largely unchanged from starting wood. For a spruce/balsam mix, the composition is 27-30% lignin, 45-50% cellulose, and 15-20% hemicellulose. Both the sodium hypochlorite and TEMPO react with lignin as well as the primary alcohol groups in both cellulose and hemicellulose. This should have an impact on the measured rates. Okita et al. have also evaluated the TEMPO reaction on thermomechanlcal pulp [86]. They obtained about 1 meq g-1 of carboxylic acid functional groups when using a 6% NaOCl charge. This is similar to Mao's outcome. But Okita showed that this continues to rise, reaching a maximum around 1.2 meq g-1 at 13% NaOCl. At NaOCl charges of 20-26 mmol g-1 the product contained virtually no residual lignin and little residual hemicellulose. The Okita data suggests that the kinetic rates determined by Mao at ul. should be

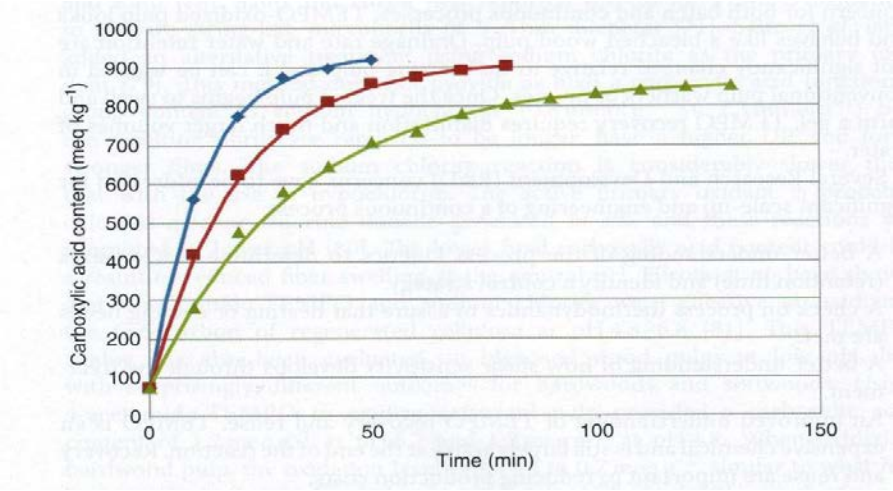


Figure 23.3 Reaction progress for TEMPO treatment of a therrnomechanical pulp. (0) 0.01 mmol kg^{-1} TEMPO charge; (I) 0.006 mmol kg^{-1}; (A) 0.002 mmol kg^{-1}.

a combined rate impacted by sodium hypochlorite consumption and reactions of the oxidized TEMPO with lignin.

Brodin and Theliander evaluated several alternative kinetic models for the TEMPO reaction with bleached wood pulp, including two shrinking core models, a first order reaction dependent on the sodium hypochlorite concentration, and a first order reaction based on the primary hydroxyl concentration [87]. They concluded that the reaction rate was nearly independent of the sodium hypochlorite concentration, which ruled out both shrinking core models and the first order model based on sodium hypochlorite. The kinetic evaluation for the homogeneous first order reaction was based on methods reported by Bragd et al. for TEMPO reactions with starch and methyl-a-D-glucopyranoside [88]. In contrast to the outcome found by Mao, Brodin and Theliander concluded the reaction of the insoluble cellulose substrate did not fit a first order model. They suggest that the reaction should be divided into three segments with the first and third segments fitting a first order assumption for primary hydroxyl groups. It appears, however, that they assumed all the primary hydroxyl groups were available to the reaction, an assumption incompatible with the known inability to completely oxidize cellulose to cellouronic acid [78]. Reevaluating the data by estimating values obtained from the graphs, and adding a factor for accessible primary OH groups, the reaction data does fit a first order model assuming that about 50% of the starting primary hydroxyl groups are accessible for TEMPO oxidation.

The sensitivity of the reaction rate to pH is shown in Figure 23.4. According to Dai et al., the rate is optimized between a pH of 10 and 11, and appears to drops off at pH above 11 [89]. The sensitivity to pH and reduction in rate at pH > 11 has also been reported for soluble sugars (77) and rayon [85].

The pH sensitivity presents a problem for continuous processing. A batch pro» cess can maintain a static pH using pH control and a metering system. In a continuous process, the pulp cannot be mixed continuously and the process will either

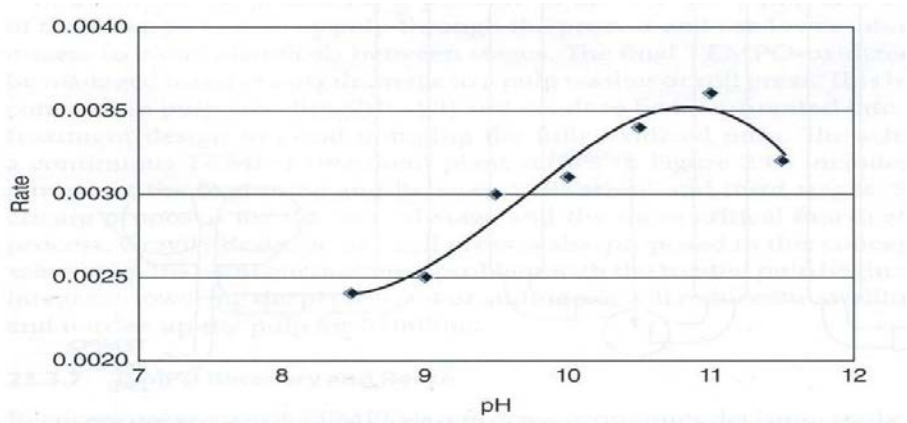


Figure 23.4 Influence of pH on reaction rate.

need to be buffered or broken into stages to enable periodic pH adjustment. For a process oxidizing pulp to about 1.6 meq g^{-1}, four equal additions that each raise the pH to about 11.6 (4 mmol NaOH g^{-1}) will neutralize the acid groups generated in the reaction, and maintain an end stage pH of 9 or above. Based on the data provided by Dai, this appears to maintain an acceptable reaction rate.

Much of the work with TEMPO treatments using sodium hypochlorite as the primary oxidant has been carried out at room temperature and Saito and Isogai have commonly used 1-2 h for the oxidation [83]. Time is capital cost in production, and many companies would opt for raising the processing temperature to reduce the volume of the equipment needed to carry out the reaction. The kinetic work of Brodin and Theliander shows that the reaction can be completed in a far shorter time, 25 min at 4-0°C or 10min at 50 °C. These are low temperatures for industrial processing and offer a big advantage to a continuous process. At 10 min retention time, even a large-scale process can be carried out in pipes, avoiding towers entirely. This becomes a plant with a very small footprint. A concept for such a plant where retention time is a series of U-shaped tubes is shown in Figure 23.5.

23.3.5 Thermodynamics

Process thermodynamics is an important consideration when increasing the scale of reactions because the need to add heat or remove heat is a critical consideration in the process, and in particular, exothermic reactions can run out of control if cooling requirements are not met. At present, there has not been a rise in temperature (exotherm) or drop in temperature (endotherm) reported for the

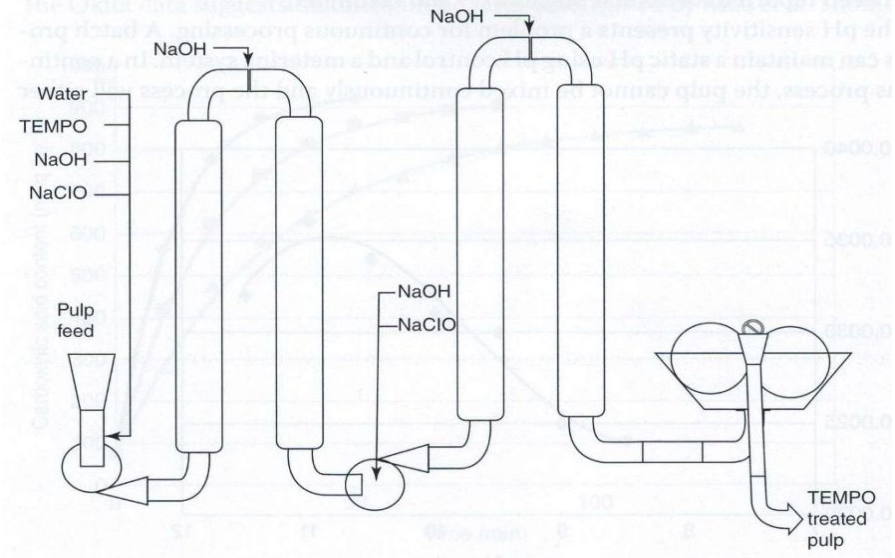


Figure 23.5 Block diagram and mass balance for a TEMPO treatment plant with TEMPO recycle.

TEMPO reaction. Typically, oxidation reaction does release heat and this does need to be accounted for in scale-up considerations. The low pulp consistency of the reaction reduces any observable temperature change, and may be sufficient for controlling temperature changes in larger scale. Furthermore, pulp bleaching is similar in using both sodium hypochlorite and sodium chlorite (chlorine dioxide) for bleaching. The exotherms in these reactions have not been large enough to cause problems.

23.3.6 Shear Sensitivity in Regards to Pumping and Mixing

Brodin and Theliander evaluated the ability to break up TEMPO-treated wood pulps after just 3 min of reaction, reporting residual long fibers (>40 mesh screen size), and average fiber length [87]. Long fiber and residual fiber length disappear at a carboxylic acid content around 1.2 meq g^{-1}. Rodionova *et al*. evaluated how much of the pulp disintegrated into a stable suspension as the reaction progressed. At 0.3-0.4 meq g^{-1}, only about 10% of the pulp breaks up sufficiently to remain in suspension after centrifuging. But at 0.8 meq g^{-1}, nearly 50% of the pulp disintegrates into a stable suspension [90].

While these results demonstrate the increasing sensitivity of the pulp to disintegrating into fibrils as oxidation progresses, they do not provide enough data on the shear sensitivity to design a process. The design question is whether the partially treated (and final) pulp can be handled in pumps and mixers without causing fiber swelling or gel formation that will complicate TEMPO recovery. Measurement of water retention after subjecting samples to known shear is needed for plant design work. The data also needs to evaluate the shear sensitivity at a variety of oxidation levels since the multiple-stage type of process will also need to provide mixing between stages. It is critical to determine the oxidation level at which the pulp begins to disintegrate in commercial centrifugal pumps and mixers. Fully oxidized pulp readily breaks in a couple hours of pump-recirculating in a tank.

In a continuous process, it is possible to use a single pump at the beginning of the reaction to convey pulp through the process and use lower intensity static mixers to blend chemicals between stages. The final TEMPO-oxidized pulp can be managed using gravity drainage to a pulp washer or roll press. This has become common in pulp bleaching [91—93] and needs to be incorporated into a TEMPO treatment design to avoid pumping the fully oxidized pulp. The schematic for a continuous TEMPO treatment plant shown in Figure 23.5 includes only two pumps, at the beginning and between the second and third stages. Static mixers are proposed for the second stage and the more critical fourth stage of the process. Gravity drainage to a roll press is also proposed in this conceptual plant schematic. Ifa plant encounters a problem with the treated pulp beginning to disintegrate, lowering the pH below 4 or adding salt will reduce the swelling pressure and harden up the pulp for handling.

23.3.7 TEMPO Recovery and Reuse

Recovery and reuse of TEMPO is a process economics decision, trading reduced operating costs for the capital costs of the recovery process. At least three

alternative methods can be considered. The simplest process collects the filtrate and recycles the sodium bromide and TEMPO remaining at the end of the process. This method has minimal capital expense, but is complicated by a significant increase in dead load salts and their impact on reaction rate, oxidation, and wastewater discharge. An alternative uses the same process idea, but employs ion exchange or possibly electrodialysis to remove the sodium chloride reaction product produced in each cycle and avoid the high ionic strength of direct recycle. A third option is solvent extraction to collect TEMPO from the filtrate. There are several other possibilities including distilling TEMPO out of the filtrate [94] and oxidizing it to the nitrosonium cation for collection by ion exchange or electrodialysis.

Mao et al. evaluated the loss in TEMPO activity by recovering the processing filtrate and reusing it. They observe about a 2% decrease per cycle in carboxylic acid content of the oxidized pulp. They do not report the effect on reaction rates, but do report extending the reactions times to consume all the sodium hypochlorite. The time increased from 50 min for the first two cycles to 55 min for the third, 60 min for the fourth, and to 70 min for the fifth cycle. There are four issues that could contribute to the declining rates:

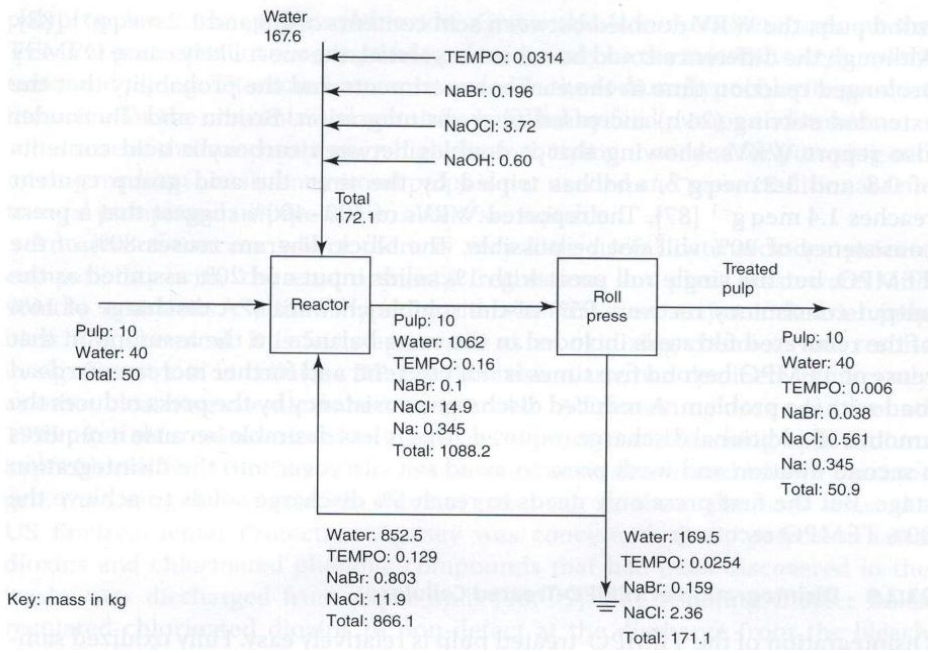
1) Loss of TEMPO to decomposition reactions
2) Loss of TEMPO in filtration and recovery, estimated at about 7% per cycle
3) Impact of increasing ionic strength on chemical activity of ions
4) Impact of ionic strength on fiber swelling and accessibility.

The change in final carboxylic acid functional group content reported by Mao *et al*. would seem to be most sensitive to the impact of ionic strength on fiber swelling. Jiang reports that increasing the sodium bromide concentration suppresses the rate of TEMPO reaction with hyaluronan, and suggested that this was shielding the negative charged hyaluronan polysaccharide chain from the nitrosonium cation. But the rate data reported does not seem to support the conclusion. In chemical kinetics and equilibrium calculations, the ionic strength influences the availability or mobility of ions for reaction, referred to as activity. The ionic strength of the experiments performed by Mao is estimated at 0.16 M for the first reaction, increasing progressively to 0.5M for the fifth cycle. The activity coefficient of monovalent ions goes through a minimum at about 0.2 M. At higher ionic strengths, the activity coefficient increases with increasing ionic strength, suggesting that the impact of the increasing sodium chloride concentration should be to increase rate. Changes in ion activity are probably not a candidate for the decrease in rate. Assuming 7% loss of TEMPO in filtration with each cycle, the combined loss after five cycles reduces the TEMPO concentration to 75% of the concentration in the first cycle. In comparison, the length of time needed to consume the hypochlorite has more than doubled. This suggests that the decrease in reaction rate is probably a combination of losses in washing and losses to decomposition.

23.3.8 Mass Balance for TEMPO Recovery

A mass balance block diagram is shown in Figure 23.6. The balance assumes 80% filtrate recovery and recycle with starting TEMPO and NaBr charges as reported

Figure 23.6 Conceptual schematic for a TEMPO treatment plant.



by Saito and Isogai *et al.* [83, 90]. The mass balance also assumes a direct recycle of process filtrate as the way to recover and reuse TEMPO. Recycle results in a salt concentration of 1.4% NaCl and 0.1% NaBr in the process filtrate and waste water. Total water requirements are 20 m3 mt^{-1} of starting pulp. At present, there is not enough information available to determine the total impact of the dead load salt on reaction efficiency. The high salt concentration does present a wastewater problem requiring stream dilution to avoid brackish conditions in the receiving water.

As stated in Section 23.3.3, TEMPO-treated pulp can be washed with traditional pulp washing or wash press equipment as long as this is performed before the pulp is subjected to significant shear that will increase swelling and water retention. In the proposed process schematic (Figure 23.5), an up-flow down-flow arrangement is used for the last two stages, with a gravity feed to a roll press. The sodium hydroxide added between the third and fourth stages is assumed to be mixed with a low shear static mixer. The schematic shows a single wash press for TEMPO recovery. With a 1% starting consistency and dewatering capability to over 25% solids, a single press can recover 95% of the TEMPO.

The assumption in the mass balance is that the roll press can dewater to over 20% solids. This is typical for pulp and paper processes, but does not factor in the change in water retention value (WRV) by TEMPO-treated fibers. Twin wire presses might be needed if the water removal is too slow for roll presses. Saito and Isogai reported WRVs for TEMPO-treated cotton in 2004, and a bleached kraft hardwood pulp in 2007. They report a fivefold increase in the WRV of cotton between a carboxylic acid content of 0.4 and 0.6 meq g^{-1} [95]. Using

wood pulp, the WRV doubled between acid contents of 0.8 and 1.2 meq g^{-1} [83]. Although the difference could be substrate related, the most likely cause is a very prolonged reaction time in the earlier experiments and the probability that the extended stirring (24 h) increased fiber disintegration. Brodin and Theliander also report \X/RVs, showing that it doubles between carboxylic acid contents of 0.8 and 1.2 meq g^{-1}, and has tripled by the time the acid group content reaches 1.4 meq g^{-1} [87]. The reported \X/RVs of 330—400% suggest that a press consistency of 20% will not be possible. The block diagram reuses 80% of the TEMPO, but the single roll press with 1% solids input and 20% assumed as the output consistency recovers 95% of the soluble chemicals. A discharge of 16% of the recovered filtrate is included in the mass balance on the assumption that reuse of TEMPO beyond five times is not efficient, and further increases in dead load salts is a problem. A reduced discharge consistency by the press reduces the amount of additional discharge required. This is less desirable because it requires a second dilution and wash press to avoid salt carryover into the disintegration stage. But the first press only needs to reach 5% discharge solids to achieve the 80% TEMPO recovery.

23.3.9 Disintegration of TEMPO-Treated Cellulose

Disintegration of the TEMPO-treated pulp is relatively easy. Fully oxidized samples (1.5 meq g^{-1}) can be disintegrated by stirring overnight with a magnetic laboratory stirrer [83]. The disintegrations have also been carried out with a kitchen blender [71, 82], sonication [71, 86], homogenizers [43, 90], a laboratory disperser [87], and a disc refiner [43]. Low-consistency refiners of the type used to condition wood pulp for paper machines can readily break up TEMPO-treated fibers and produce a translucent gel. Refiner plates with surface dams and operated at narrow plate clearance work well [43]. There is considerable mechanical heating from homogenizers and refiners, and this must be accounted for in commercial-scale design. The very best, clear suspensions with no residual material large enough to reflect light or contribute to haze cannot be achieved with pulp refiners and many of the other devices used in laboratory research including ultrasound treatments. Homogenizers do provide the high level of clarity required for demanding optical applications, but the very high pressures needed to achieve it result in significantly shorter valve and seal life and high maintenance requirements. While the rest of a TEMPO treatment plant is similar to pulp mill bleach plants and chemical process technologies and should be able to operate with very high availability and low maintenance, homogenizers will not offer that level of reliability.

23.3.10 Other Commercial Plant Concerns

The combination of the high salt concentration and high sodium hypochlorite concentration is a demanding materials environment for metals. Stress corrosion cracking is a problem for 316 and 317 stainless steel at high salt concentrations. The sodium hypochlorite product literature does not recommend stainless steel or more corrosion-resistant alloys including the Hastelloy®and Monel® alloys. Several polymers are considered suitable including fiberglass, polyethylene,

polypropylene, and polyvinylchloride. Given the lower temperatures of the TEMPO pretreatment process, these polymers may be the safest choice for plant tanks and piping. Titanium is recommended in the sodium hypochlorite product literature for the concentrated solutions handled by feed pumps and mixers.

Because of the low consistency, high shear equipment needed for pumping and mixing medium consistency wood pulps is not needed and more traditional centrifugal pumps and in-pipe static mixers are suitable.

An area of concern where there is very little useful data includes process compatibility with the environmental regulations on plant wastewater and volatile emissions. Sodium hypochlorite was the first major industrial pulp bleaching chemical. It is fairly aggressive as an oxidizing chemical and results in significant loss in cellulose DP. For this reason, use had declined significantly as other bleaching chemicals became available. All remaining use ended around 1995 after chloroform was identified as a by-product of bleaching with sodium hypochlorite [96, 97]. As a fairly volatile organic molecule and known carcinogen, managing the chloroform was not practical. At about the same time, the US Environmental Protection Agency was concerned about polychlorinated dioxins and chlorinated phenolic compounds that had been discovered in the wastewater discharged from paper mills [98, 99]. The resulting Cluster Rules regulated chlorinated dioxins to non-detect at the discharge from the bleach plant, and chlorinated phenolics to very low levels- also monitored at the exit of the bleach plant. Similar discharge restrictions were put in place in Europe and Canada. In responding to the new restrictions, the paper industry abandoned molecular chlorine and sodium hypochlorite and switched to performing nearly all bleaching with chlorine dioxide and peroxide [99].

Whether chloroform or other chlorinated hydrocarbons are going to be a concern with sodium hypochlorite oxidation of TEMPO is not known. The source of both chloroform and chlorinated phenols is thought to be from the residual lignin polymer in unbleached wood pulp, and not the cellulose or hemicellulose. But that is not known with certainty. Before moving forward with a large-scale TEMPO treatment plant, it will be necessary to test volatile emissions and the aqueous waste for chlorinate hydrocarbons

23.4 Status Summary

Over that last decade, there has been considerable interest in the production and use of nanoparticles from cellulose. There has been good progress in understanding the various particle forms and working with both the traditional methods and newer concepts to adjust the particle forms. There has not been as much progress on useful and cost-effective applications, although several commercial-scale applications have been started in the last 2 years. Enough is known about these materials for a company to make a bold move into large-scale production, once a market is obvious. We have seen several companies expand to the 5 mt per day scale. The next round of expansions is going to have to address some of the difficult engineering questions remaining including the

environmental questions and developing continuous processing alternatives. This is an industry poised to happen. It may end up as an extension of the existing paper industry or, more likely, an entrepreneurial company aligned with higher value applications. But the process — production of the cellulose nanoparticle intermediate - is ready for products.

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