Effects of cellulosic nanofibrils on papermaking properties of fine papers

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ABSTRACT: Cellulosic nanofibrils (CNF) were produced in a disk refiner, to various fines contents. This material was used as an additive to papermaking furnish at laboratory and pilot scales. Handsheets showed improved strength and surface properties with the addition of CNF. Properties also tended to improve with increasing fines content of CNF. Desired strength properties were achieved using CNF at different fines contents by adjusting the loading levels of CNF. On a pilot scale, CNF allowed an increased ash level while maintaining control properties. Strength and surface properties were generally enhanced with use of CNF, although drainage properties were adversely affected. Machine runnability was good, even at higher CNF dosages and slower drainage. CNF in the sheet appears to increase press solids.

Application: Refiner-produced CNF can be used in fine papermaking to improve filler retention and enhance paper properties, particularly surface characteristics.

The papermaking industry has shown an interest in the manufacture and use of cellulosic nanofibrils (CNF), commonly referred to as nanocellulose. In a review of published literature on the use of CNF as a paper additive or coating material, Brodin and coworkers [1] found research indicating that CNF in paper enhances dry strength properties by increasing the bonded area and density of the sheet. This would also decrease air permeability through the sheet. CNF was also found to bind more filler particles in the sheet while retaining the strength properties. Some of the articles reviewed also indicated that although CNF addition would adversely affect drainage on the paper machine, this could be counteracted with a properly chosen retention aid system [1].

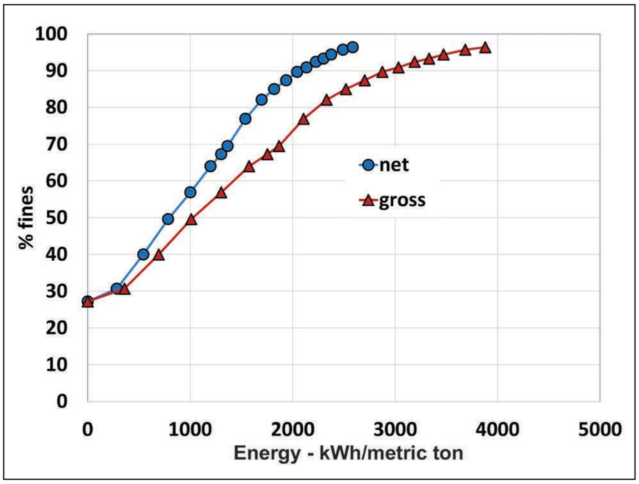
Kajanto and Kosonen used 1%-2% nanofibrillar cellulose (NFC) manufactured at UPM-Kymmene's pilot facilities in Finland as a reinforcement agent in 50-65 g/m² paper produced on a high-speed pilot machine [2]. They reported good machine runnability and enhanced paper strength with the addition of nanocellulose to the paper furnish. They also reported an unexpected increase in press solids [2]. This increase has also been found during a separate pilot trial at VTT Technical Research Centre of Finland [3].

Work previously cited uses a variety of mechanical methods (grinding, homogenization, microfluidization) to produce nanocellulose, with or without pretreatments. However, none of the studies used disk refining. The CNF production facility at the University of Maine Process Development Center (UMaine PDC; Orono, ME, USA) can produce 1 ton/day of CNF, using a multi-stage disk refining process (with no pretreatment). This is the same process being used at the Paperlogic mill in Turners Falls, MA, USA, which started production in May 2015 [4]. Using a refining process to make nanocellulose (rather than grinding, microfluidization, or homogenization in combination with chemical treatments) offers the advantages of a more energy-efficient and easily scalable process.

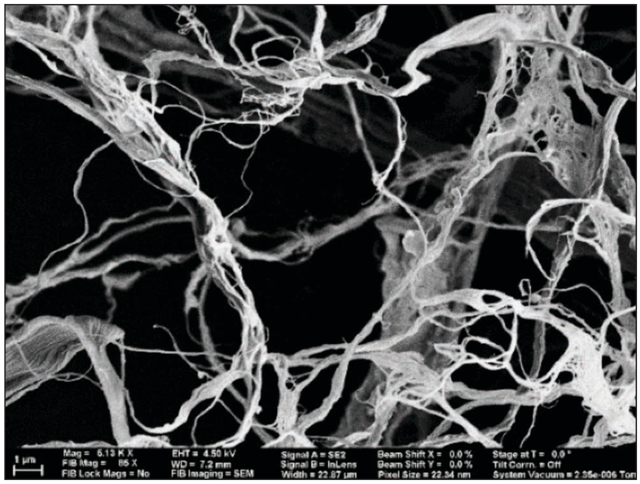
Several groups are working on the development of highly refined pulps using refiner technology. The continuum of refining begins with refining to produce refined pulp for papermaking stock. Further refining produces microfibrillated cellulose. Extended levels of refining produce very highly refined cellulose with nanoscale elements, or CNF. Product naming has yet to become standardized, so actual dimensions and characteristics of material produced might be unique to the producer.

A 2008 patent issued to Japan Absorbent Technology Institute [5] describes a production method for microfibrillated cellulose to be used particularly as a bonding agent and dispersion agent for highly absorbent polymers in such products as sanitary articles using highly absorbent polymers. The production method is described as multi-stage disk refining, recirculating the pulp through the refiner(s) multiple times until the desired particle size and water retention characteristics are achieved.

A 2014 U.S. patent application [6] describes the production of surface-enhanced pulp fibers, which are fibers with greatly increased surface area but relatively low fines content. These fibers are made with multiple passes through disk refiners, using energies of 300-650 kW·h/ton. The patent states that fibers can be used in pulp, paper, paperboard, and bio-



1. Energy required to reach various fines contents in cellulosic nanofibrils (CNF).



2. Scanning electron microscope image of CNF at 90% fines content, 6000× magnification.

fiber composites, and in other applications [6]. A 2015 patent [7] discloses a method to produce nanocellulose using a conical refiner.

We have undertaken studies using refiner-produced CNF in the production of paper. This work has involved handsheet studies, pilot paper machine trials, and commercial production.

EXPERIMENTAL

CNF production

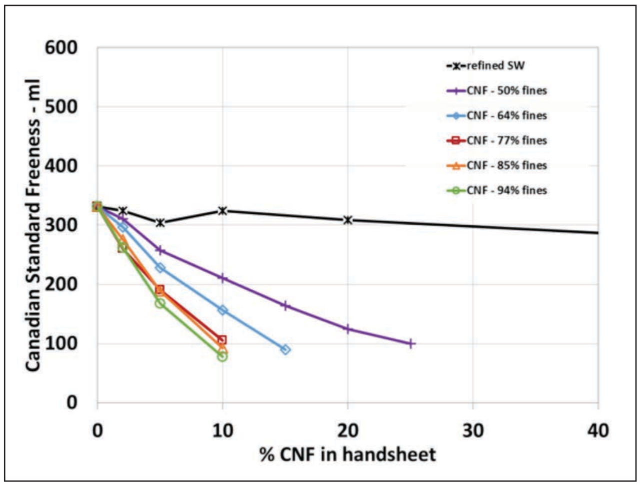
The CNF used in all phases of the work reported here was produced at UMaine PDC's Cellulose Nanofibril Pilot Plant. It was produced from northeastern bleached softwood kraft pulp using a 20 in. GL&V refiner and a two-stage process. The pulp was refined to various energy levels, resulting in CNF with different fines contents. Fines content was measured with a MorFi fiber analyzer (Techpap; Grenoble, France), set up to measure fines content as material below 0.2 mm. **Figure 1** shows the energy required to reach various fines contents.

These energy-fines curves vary depending on refiner process conditions and on the pulp used as a feedstock. In other work [8], CNF made with hardwood as a feedstock take less energy to achieve a given fines content. However, the quality between the hardwood and softwood CNF differs at the same fines content. When used as a 2%-10% additive to hardwood base pulp in handsheets, hardwood CNF at a given fines content gave lower tensile, porosity, and bond values to the handsheets than softwood CNF at the same fines content. This quality difference diminished as the fines content of the CNF rose, and at 90% fines content, the properties in handsheets of hardwood and softwood CNF were very similar.

Figure 2 illustrates the softwood CNF produced for these studies.

Handsheet studies

Handsheets were made with bleached northern hardwood pulp refined to 330 mL Canadian Standard Freeness (CSF) as a base. Using CNF with different fines contents, handsheets were made at several CNF loadings (as a percentage of total fiber). Handsheets were also made with added bleached softwood at loadings comparable to the CNF additions. **Table I** summarizes the results of handsheets tested for a range of properties using standard procedures.



3. Canadian Standard Freeness (CSF) of handsheets over a range of CNF loadings, and at different CNF fines levels.

Adding CNF to the handsheets slows the drainage of the sheet. **Figure 3** plots freeness values, showing that the freeness of the pulp is little changed with the addition of refined softwood. With the addition of any CNF, the freeness decreases. The degree of the decrease depends on the fines content of the CNF. As the CNF fines content increases at a given CNF loading, the freeness decreases. This decrease is much less pronounced at the higher CNF fines level, as seen in the very similar 77%, 85%, and 94% CNF fines content curves. In this data set, the final CNF loading of each CNF fines level curve resulted in a freeness close to 100 mL CSF. To reach that freeness, it took 10% of the higher fines content CNF, 15% of the 65% fines content CNF, and 25% of the 50% fines content CNF.

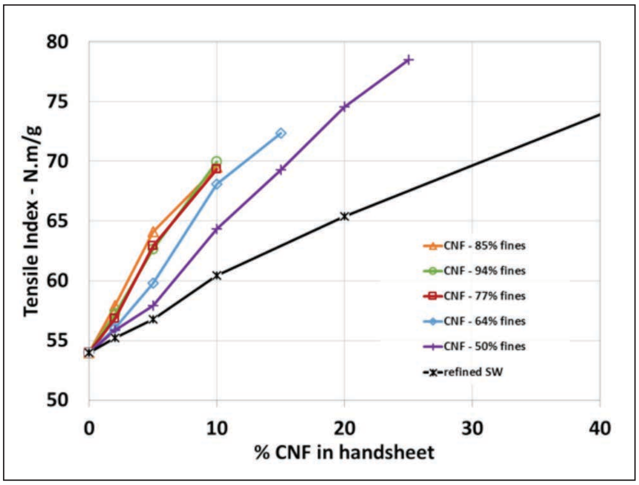
% Fines in CNF	% Fines in CNF	CSF, ml	WRV g Water/ g Dry Pulp	Shrinkage, %	Bulk, cm^3/g	Tensile Index, Nm/g	Tear Index, $mN.m^2/g$	Internal Bond, kg.cm	Gurley Porosity, Gurley sec	Sheffield Roughness (plate), Sheff. Units
	0	332	2.2	5.1	1.387	54.0	8.1	1.89	28	127
Refined softwood	2	324	2.2	5.3	1.429	55.2	8.4	1.83	28	125
	5	305	2.2	5.2	1.436	56.8	8.4	2.06	30	126
	10	324	2.3	5.2	1.364	60.5	9.0	1.94	34	124
	20	309	2.3	5.6	1.363	65.4	9.5	2.31	48	115
	100	222	2.6	7.0	1.303	99.6	10.4	3.49	467	76
50	2	311	2.2	5.2	1.434	55.9	8.0	1.97	31	125
	5	258	2.4	5.5	1.363	57.9	8.0	2.23	51	104
	10	211	2.4	6.0	1.317	64.3	8.4	2.59	95	94
	15	164	2.6	6.7	1.317	69.3	8.3	2.72	175	69
	20	125	2.6	7.0	1.282	74.5	8.6	3.30	298	61
	25	100	2.8	7.1	1.267	78.5	8.9	3.55	535	44
64	2	297	2.3	5.4	1.365	56.0	7.9	2.09	44	113
	5	228	2.4	5.8	1.354	59.8	8.1	2.18	68	96
	10	156	2.6	6.5	1.318	68.1	8.3	2.55	158	79
	15	90	2.8	7.3	1.277	72.4	8.3	3.10	321	51
77	2	260	2.4	5.5	1.386	56.8	8.2	1.98	36	113
	5	190	2.4	6.0	1.321	62.9	8.3	2.29	91	85
	10	105	2.7	6.9	1.319	69.3	8.4	2.48	247	63
85	2	276	2.3	5.2	1.370	57.9	7.8	1.88	43	107
	5	189	2.5	5.9	1.320	64.1	8.4	2.01	94	92
	10	92	2.7	6.7	1.270	69.5	8.6	2.69	344	61
94	2	262	2.4	5.3	1.355	57.2	8.4	2.01	49	106
	5	168	2.5	6.0	1.325	62.6	7.7	2.60	104	83
	10	78	2.8	7.1	1.280	70.0	8.3	3.12	365	60

I. Handsheet properties.

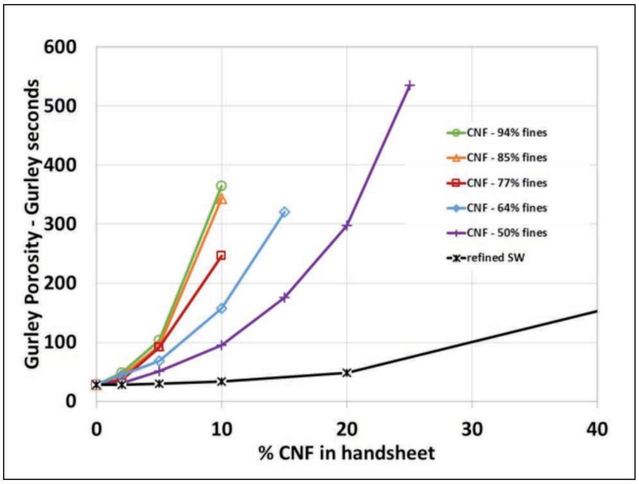
Shrinkage and water retention value data show trends similar to the freeness data (Table I).

Figure 4 shows the tensile index of the handsheets. Tensile value increases by increasing softwood or CNF loading in the handsheets and by increasing the fines content of the CNF at a given loading. As with the freeness data, the difference between the higher levels of fines in the CNF is minimal. A similar tensile index can be achieved by adding different amounts of CNF at different fines contents. For example, it would take about 3% of the 77% fines CNF to reach a tensile index of 60 N·m/g, and about 7% of the 50% fines CNF to reach the same tensile strength, or 10% of the refined softwood.

Surface properties of the handsheets are also affected by the addition of CNF. Sheffield roughness values, which decrease only slightly with the addition of softwood to the hardwood furnish, decrease more noticeably with the addition of CNF (Table I). As with the strength properties, an increase in both CNF loading and CNF fines content decreases roughness



4. Tensile index of handsheets over a range of CNF loadings, and at different CNF fines levels.



5. Porosity of handsheets over a range of CNF loadings, and at different CNF fines levels.

values. **Figure 5** shows that Gurley porosity values increase greatly with increasing amounts of CNF in the handsheets; higher fines levels of CNF sharply increase the sheet closure.

The previous data have indicated that targeted handsheet properties can be obtained by including CNF in the handsheet furnish at different loading levels, and by changing the fines level of the CNF added to the furnish. To illustrate this effect, a target tensile value of 10% above that of the hardwood base sheet was chosen as the reference point. For each of the CNF fines contents, testing determined the loading at which this tensile value was obtained. The remaining properties were then interpolated at that loading level. **Table II** shows this data.

Adding 8.5% softwood to the base sheet gives this 10% increase in tensile index. With the addition of softwood, several changes occur: freeness and roughness are minimally affected, tear increases slightly (because of the softwood fiber length contribution), porosity increases by 18%, and internal bond increases by 5%.

The amount of CNF needed to achieve the 10% increase in tensile target is 6% for the 50% fines content CNF, which decreases to 5% for the 65% fines content CNF. The 75%, 85%, and 95% fines content CNF require ~3% CNF addition to get to the target tensile value. Adding CNF at any fines content decreases the freeness by ~30%. Tear index remains unaffected. In most cases, internal bond increases at the target tensile value, while roughness decreases by ~20% with CNF addition. Gurley porosity is greatly increased at the target tensile value with CNF addition, with a 100%-150% increase over the base sheet value.

Handsheet study conclusions

The handsheet work shows that strength and surface properties improve with the addition of CNF, and with the addition of increasing fines content in the CNF. The decrease in drainage properties might be addressable with chemistry.

Similar property values can be reached by either adjusting CNF loading levels or CNF fines content. Less difference is seen in handsheet properties using CNF with between 77% and 94% fines. Although this might hold for paper properties, CNF within this range of fines contents show rheological differences that might be important for the use of CNF in other industries.

Pilot paper machine studies

Pilot paper machine trials have been conducted on the UMaine PDC pilot machine, a fourdrinier machine with a 13 in. trim, run at 80 ft/min for the filled 75 g/m² sheet chosen. The base furnish used was a northern bleached hardwood pulp base stock refined to ~380 ml CSF, with 15 lbs/ton starch and 0.4 lbs/ton cationic polyacrylamide flocculant (Percol 175; BASF, Ludwigshafen, Germany) added to all furnish. Bleached softwood kraft CNF at varying fines contents was added to the base sheet at varying rates. At each dosage of CNF, ground calcium carbonate was added at several levels (16%-32%). As a control, ground calcium carbonate alone (with no CNF) was added to the base sheet over a similar range of dosage levels.

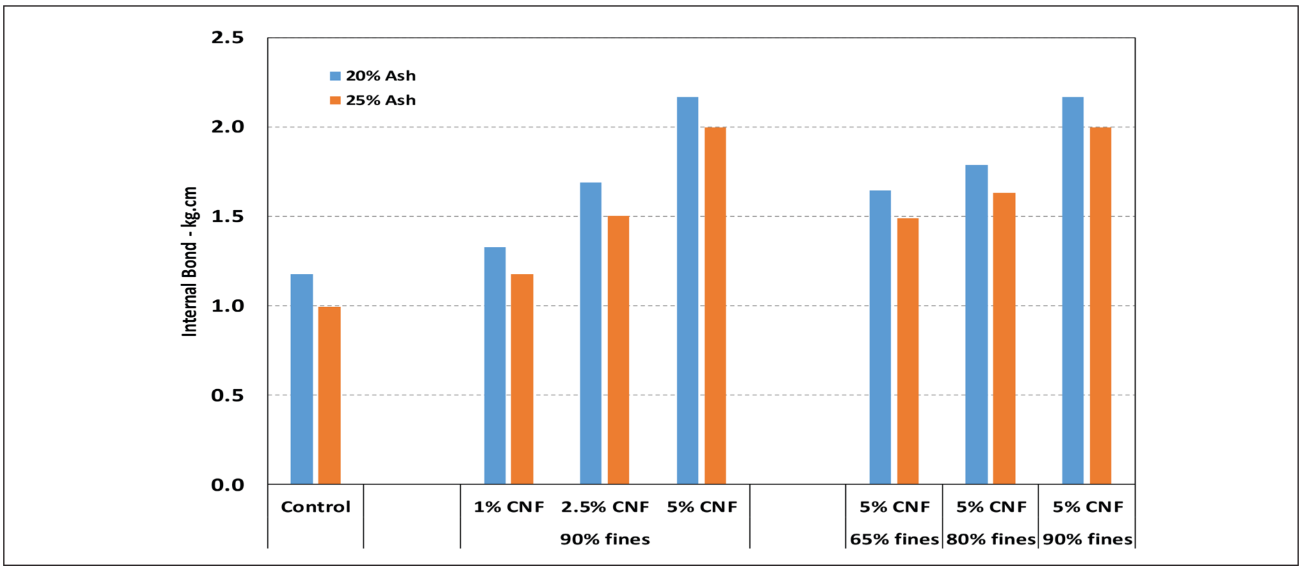
Samples of paper at each ash and CNF condition were collected and tested. Data were analyzed and normalized to comparable ash content in the paper. **Table III** shows the paper properties at sheet ash contents of 20% and 25%. Each ash level has two sets of data. One set is for 90% fines content at

% Fines of CNF	% CNF	Tensile Index, N.m/g	CSF, ml	Tear Index, mN.m³/g	Gurley Porosity, Gurley sec	Sheffield Roughness, Sheff. Units	Internal Bond, kg.cm
Hardwood base sheet		54.0	332	8.1	28	127	1.88
SW	8.5	59.4	318	8.8	33	125	1.98
50	6.1	59.4	247	8.1	61	102	2.31
65	5	59.8	228	8.1	68	96	2.18
75	3.3	59.4	230	8.2	60	100	2.11
85	2.7	59.4	255	8.0	55	103	1.91
95	3.2	59.4	223	8.1	72	97	2.26

II. CNF-containing handsheet properties at a tensile value of 10% above the hardwood base sheet tensile value.

		Sheet Ash, %	Ash Retention, %	CSF, ml	Press Solids, %	Bulk, cc/g	Internal Bond, kg.cm	MD Tensile Index, Nm/g	CD Tensile Index, Nm/g	Sheffield Roughness, Sheff. Units (felt)	Gurley Porosity, Gurley Units
Properties @ 20% Sheet Ash											
	Control	20	77.8	380	46.8	1.42	1.18	39.9	18.0	148	9
90% fines	1% CNF	20	84.2	303	46.3	1.33	1.33	43.6	19.0	147	13
	2.5% CNF	20	84.4	241	45.7	1.36	1.69	46.6	21.4	133	20
	5% CNF	20	88.0	134	50.5	1.25	2.17	53.2	24.0	132	35
65% fines	5% CNF	20	82.9	251	46.4	1.29	1.64	42.5	20.5	126	22
80% fines	5% CNF	20	90.2	206	47.6	1.28	1.79	44.1	20.9	127	26
90% fines	5% CNF	20	88.0	134	50.5	1.25	2.17	53.2	24.0	132	35
Properties @ 25% Sheet Ash											
	Control	25	76.8	376	47.1	1.40	0.99	33.8	15.2	137	9
90% fines	1% CNF 90%	25	83.7	305	46.8	1.29	1.18	36.6	17.1	137	12
	2.5% CNF 90%	25	84.2	232	48.4	1.32	1.50	40.1	18.1	124	19
	5% CNF 90%	25	86.6	132	50.4	1.24	1.99	45.1	20.7	123	35
65% fines	5% CNF 65%	25	84.3	253	47.2	1.26	1.49	39.0	18.1	116	20
80% fines	5% CNF 80%	25	88.4	204	49.2	1.27	1.63	38.5	18.3	118	24
90% fines	5% CNF 90%	25	86.6	132	50.4	1.24	1.99	45.1	20.7	123	35

III. Pilot machine paper properties at 20% and 25% ash levels.

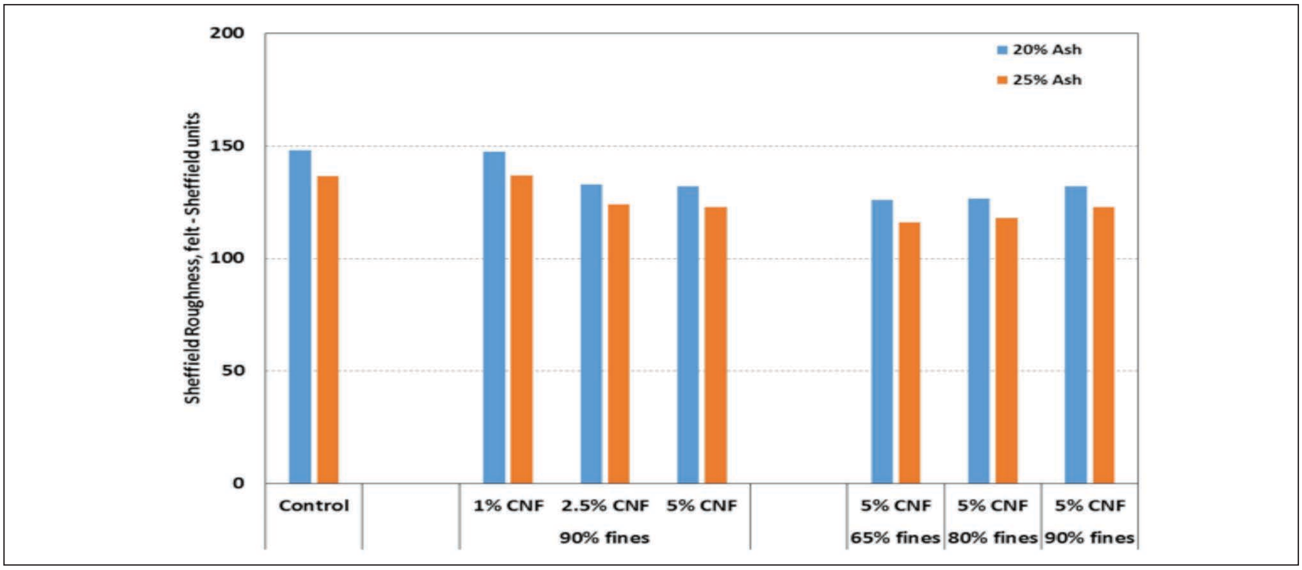


6. Internal bond values of pilot machine paper at 20% and 25% ash loading.

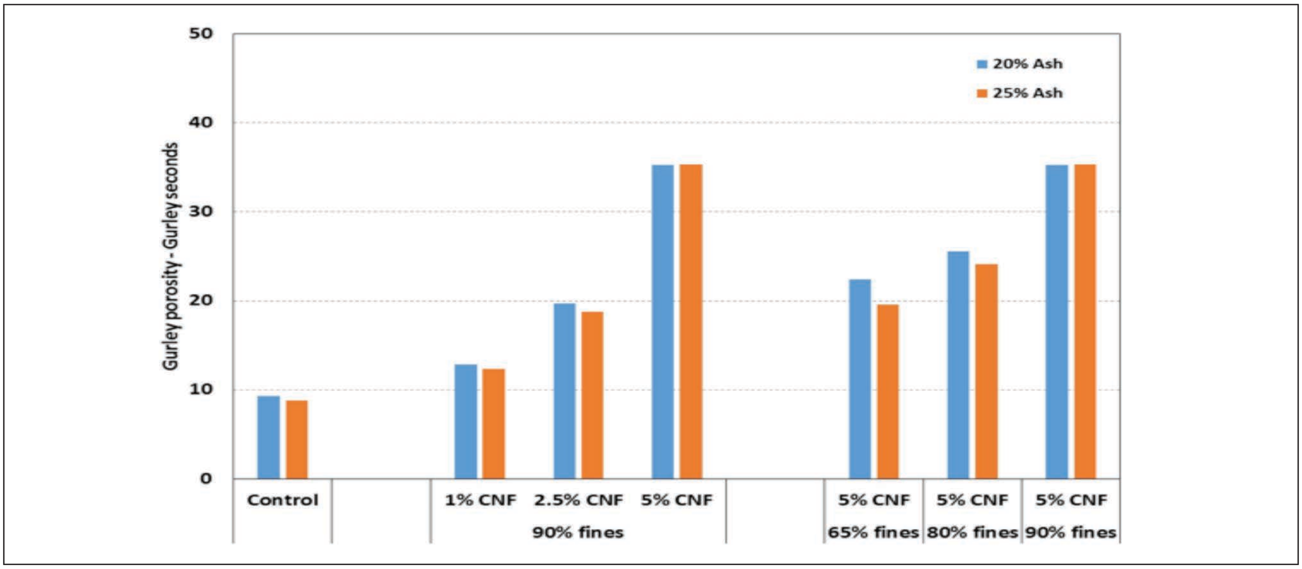
1%, 2.5%, and 5% CNF loading (fixed fines content at various loadings). The other set is for 5% loading of 65%, 85%, and 90% fines content CNF (fixed loading at various fines contents).

Property trends for the pilot machine-made paper tend to follow the results of the handsheet studies. Headbox freeness decreases with increasing CNF loading of 90% fines content CNF, and with increasing fines content CNF at 5% loading, at all ash levels. With an increasing amount of 90% fines content CNF in the sheet, the tensile index increases for both 20% and 25% ash levels (Table III). At 5% CNF loading, the tensile index increases with increasing fines content of the CNF. This same pattern is seen for internal bond (**Fig. 6**).

Figure 7 shows that the sheet smoothness increases (and



7. Roughness values (felt side) of pilot machine paper at 20% and 25% ash loading.



8. Porosity values of pilot machine paper at 20% and 25% ash loading.

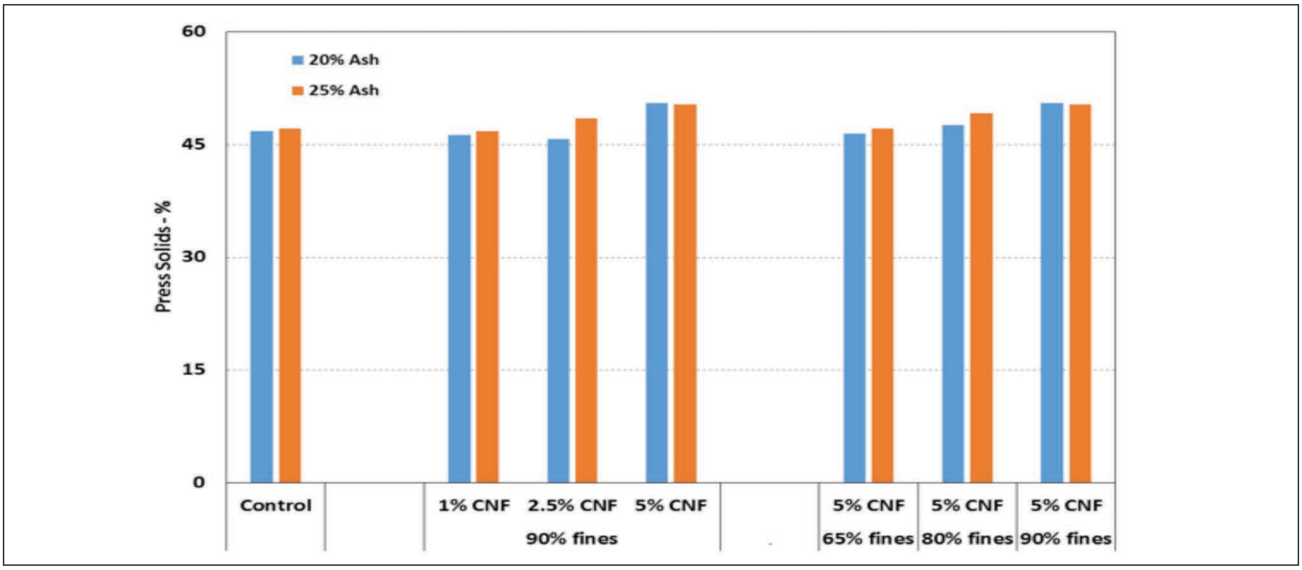
roughness decreases) with increasing 90% fines content CNF. The fines content of the CNF at 5% loading makes less difference in the smoothness of the sheet than does the loading level of CNF.

Porosity is a measurement of the time needed for a set volume of air to pass through the sheet. **Figure 8** shows that porosity values increase with increasing 90% fines content CNF and increase sharply as loading levels reach 5% CNF. Porosity values also increase at the 5% loading level as the fines content of the CNF increases. This indicates a tightening of the sheet, or increasing porosity value, with both increasing CNF loading and increasing CNF fines level.

As seen by other researchers [2,3], press solids increase with increasing levels of 90% fines content CNF, and with increasing fines content CNF at 5% loading (**Fig. 9**).

Adding CNF to the sheet makes it possible to increase the ash level of the sheet while maintaining other properties. Using the control condition of 15% filler as the reference strength level, we made calculations to determine the amount of filler that could be added to the sheet to maintain the reference strength value when CNF was also added to the sheet. **Table IV** shows where first the internal bond is held to a constant level, and where the machine direction tensile index is held constant. From there, the other properties are interpolated or extrapolated to that point.

Bond was seen to increase significantly with increasing amounts of 90% fines content CNF (Fig. 6), so the calculated allowable levels of ash also rose significantly. At 2.5% CNF loading of 90% fines content CNF (Table IV), ash levels could rise from the 15% control level to 29%, while maintaining the



9. Press solids values of pilot machine paper at 20% and 25% ash loading.

	Sheet Ash, %	Δ in Sheet Ash	Ash Retention, %	CSF, ml	Press Solids, %	Bulk, cc/g	Internal Bond, kg.cm	MD Tensile, Nm/g	CD Tensile, Nm/g	Sheffield Roughness, Sheff. Units (felt)	Gurley Porosity, Gurley sec
Ash Increase to Maintain Control Bond @ 15% Ash											
Control	15	15	79	383	46.4	1.43	1.36	46.0	20.7	159	9.7
1% CNF 90%	19	4	84	303	46.2	1.34	1.36	45.0	19.3	150	13
2.5% CNF 90%	29	14	84	225	50.6	1.28	1.35	34.8	15.5	117	18
5% CNF 90%	43	28	81	125	49.8	1.21	1.37	15.8	8.6	90	36
5% CNF 65%	29	14	85	255	47.8	1.24	1.37	36.2	16.2	108	17
5% CNF 80%	34	19	85	199	52.1	1.26	1.35	33.8	13.7	103	22
5% CNF 90%	43	28	81	125	49.8	1.21	1.37	15.8	8.6	90	36
Ash Increase to Maintain Control Tensile @ 15% Ash											
Control	15		79	383	46.4	1.43	1.36	46.0	20.7	159	9.7
1% CNF 90%	18	3	84	302	46.1	1.34	1.39	46.4	19.7	152	13
2.5% CNF 90%	20	5	84	241	45.7	1.36	1.69	46.6	21.4	133	20
5% CNF 90%	24	9	87	133	50.4	1.24	2.03	46.7	21.3	125	35
5% CNF 65%	15	0	82	249	45.7	1.32	1.80	46.1	23.0	136	25
5% CNF 80%	17	2	91	207	46.6	1.28	1.88	46.3	22.4	132	26
5% CNF 90%	24	9	87	133	50.4	1.24	2.03	46.7	21.3	125	35

IV. Pilot machine paper: ash increase possible with added CNF, while maintaining bond or tensile values at control 15% ash level.

same internal bond. Tensile index decreases with the increasing ash level, but smoothness and porosity are higher than the control. Even the lower CNF loading level of 1% of the 90% fines content CNF allowed for a 4 percentage point increase in ash level (from 15% to 19%), with minimal loss in tensile strength (from 46 N·m/g to 45 N·m/g), and some increase in smoothness and porosity.

While maintaining the target bond level, the sheet ash could be increased at the 5% CNF loading level using CNF with different fines contents. The 65% fines content CNF allowed 14% more ash into the sheet, increasing from 15% to 29% ash. Tensile index decreased, while smoothness and porosity increased substantially.

To maintain the machine direction tensile index of the control at 15% ash, 46 N·m/g, adding 90% fines content CNF at 5% loading allows ash to rise to 24%. Bond increases substantially, from 98 to 146 ft·lb/1000 in^2, roughness decreases from 159 to 125 Sheffield units, and porosity increases from 10 to 35 Gurley seconds.

Pilot machine trial conclusions

CNF allows an increasing ash level in the sheet while maintaining control properties (no CNF, lower ash). Strength and surface properties are generally enhanced with use of CNF, although drainage properties are adversely affected. Machine runnability was good, even at higher CNF dosages and slower drainage. CNF in the sheet appears to increase press solids. **TJ**

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ABOUT THE AUTHORS

The UMaine Process Development Center (Orono, ME, USA) has a pilot CNF production facility, as well as a pilot-scale paper machine, so we are well situated to explore the benefits of CNF use in paper.

Much of the previous published research using CNF in paper had used CNF manufactured using different processes than the refiner method used in this work. The refiner production of CNF is more scalable and economical than many production methods.

Previous work by others has shown an increase in press solids with the use of CNF internally. We also saw this in some cases, but have not yet been able to confirm under what conditions this happens.

Next steps are under way, and include more work with CNF internally within the sheet, as well as the surface application of CNF on the sheet. We're also looking at CNF use in other paper grades, including board grades.

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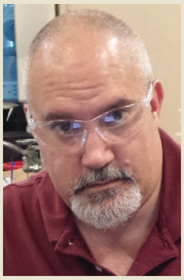

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