Wet-end addition of nanofibrillated cellulose pretreated with cationic starch to achieve paper strength with less refining and higher bulk

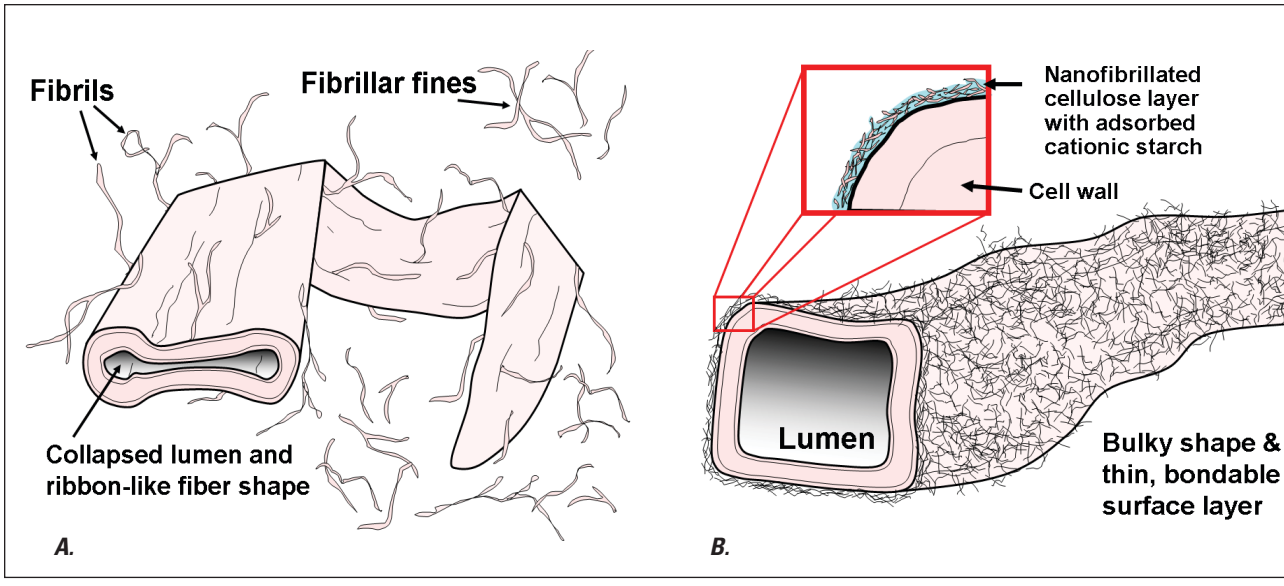
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ABSTRACT: Nanofibrillated cellulose (NFC) treated with cationic starch was evaluated as a bonding system to permit lower degrees of refining and lower apparent density of high-mass handsheets made from bleached kraft pulp. Mixed pulp (70% hardwood, 30% softwood) was formed into sheets with the optional addition of 5% by dry mass of NFC. The default addition of NFC was compared with a system in which the NFC had been pretreated either with cationic starch (at various levels) or optionally followed by colloidal silica. Comparative tests also were carried out with separate addition of cationic starch to the main furnish. Unrefined fibers (514 mL CSF) were compared with low-refined (473 mL CSF) and high-refined (283 mL CSF) pulp mixtures. The NFC that had been pretreated with cationic starch at a high level was especially effective at boosting the tensile strength and stiffness of sheets prepared from pulp that had been refined at a low level, thus achieving improved strength at relatively low apparent density (high bulk) of the handsheets. The results support a strategy, for applicable grades of paper, of using cationic starch-pretreated NFC in place of refining energy applied to the main fiber furnish. It was further established that colloidal silica can be employed as a further pretreatment of the cationic starch–treated NFC as a means of promoting dewatering in the combined system.

Application: Higher caliper at a defined basis weight, while maintaining tensile strength and stiffness, can be achieved by use of cationic starch–pretreated nanofibrillated cellulose, while decreasing the main refining of kraft fibers. Mills can consider this technology for paper and board grades for which low apparent density and maintaining stiffness are primary goals.

In the manufacture of paper and paperboard, it can be difficult to maintain specified strength levels while minimizing fiber costs and meeting specified targets for caliper [1,2]. Refining of the pulp is generally regarded as a primary tool by which to enhance bonding within paper. However, excessive refining tends to slow the dewatering rate during the paper forming process, and the resulting paper tends to be denser [3,4]. If substantially increased bonding could be achieved without as much refining of the main furnish, then it might be possible to achieve paper property targets—including caliper and stiffness targets—at lower basis weights. Also, a wet web composed of less-refined fibers can be expected to exhibit greater recovery of its thickness (caliper) when exiting from a wet-press nip [5,6]. Thus, the combination of lower-refined fibers, possibly a lower amount of fibers per a given area of product, and enhanced bonding has the potential to decrease the amount of evaporative energy needed to dry paper as it is being made. Such technology would also be of great interest to papermakers who rely strongly on the use of recycled fibers, which often have less capacity to be improved by refining. For instance, Delgado-Aguilar et al. [7] demonstrated that highly fibrillated cellulose can be effective as a bonding agent in furnish composed of recycled fibers. Paper grades that are likely to benefit from the ability to achieve strength properties at lower apparent density would include return postcard stock, book paper, paper towel, folding boxboard, and various specialty products.

Micro- and nanofibrillated cellulose (MNFC) has been considered in past studies as a papermaking wet-end additive [8–12]. Though such addition of nanocellulose to papermaking furnish has been shown to increase paper strength, it also tends to slow the rate of dewatering [13], which is often a key factor affecting the speed of production. However, most such studies have not involved the usage of cationic starch or other cationic polymers. An exception was the work of Ahola et al. [14]. Those authors pretreated the main cellulosic pulp fibers with a high-mass, high-charge wet-strength polymer, polyamidoamine-epichlorohydrin, followed by the addition of NFC. A dense layer of NFC was collected onto the fiber surfaces by that approach. When the cationic polymer was instead used



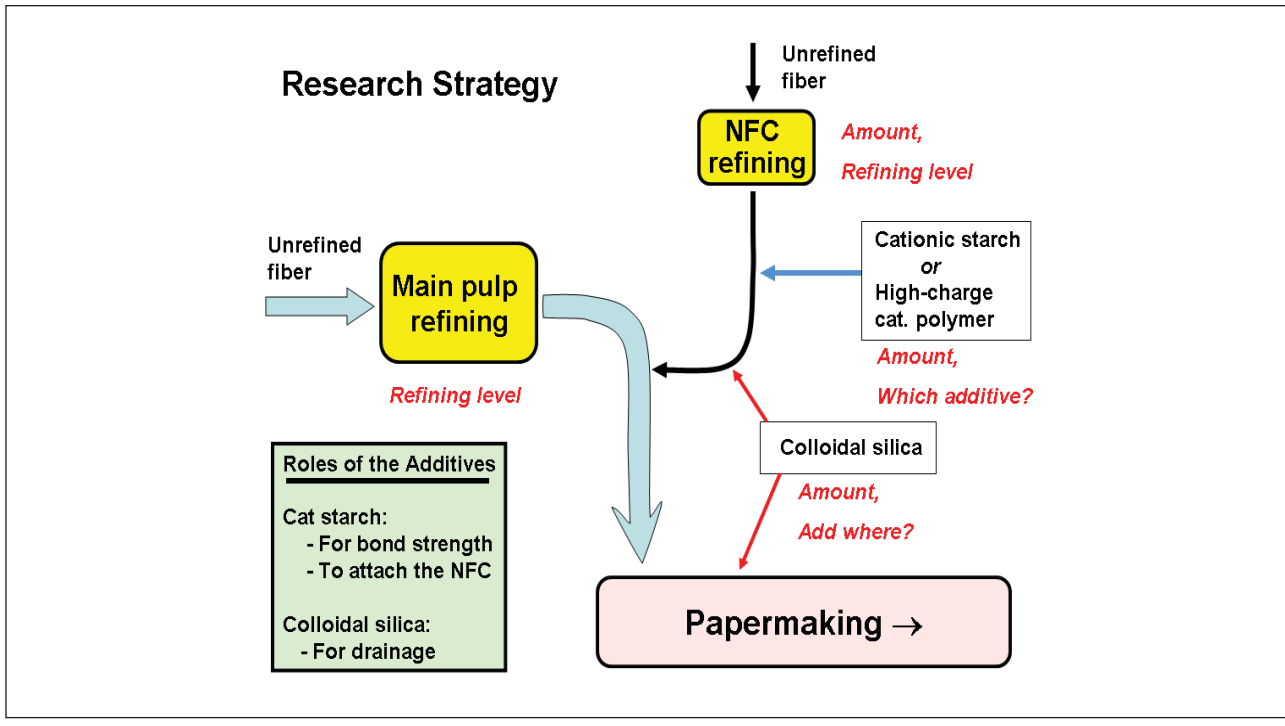
1. Illustration of a contrast in fiber cross-sectional shape (ribbonlike versus tubelike) and fines content when comparing (A) conventional refining and (B) placement of pretreated nanofibrillated cellulose (NFC) at the surfaces of lower-refined fibers.

to pretreat the NFC, excessive agglomeration occurred, which may have been a result of the high molecular mass and charge density. Increases in paper strength were observed, especially when sequentially adding the cationic polymer and NFC to the furnish. More recently, Merayo et al. [15] found synergistic relationships between the use of NFC and certain cationic polymers. Likewise, Hollertz et al. [16] showed that favorable strength benefits were achieved when certain NFC preparations were added together with polyvinyl amine, a strongly cationic polymer.

The main hypothesis underlying this work can be understood from the diagrams in **Fig. 1**. The image at the left represents a conventionally well-refined kraft pulp fiber in the wet state. As is well known [17], sufficiently high levels of refining promote internal delamination in the fiber walls, such that the fiber lumens are able to collapse, giving rise to a ribbonlike fiber shape. The ribbonlike, conformable fibers resulting from extensive refining enable development of strong interfiber bonding, relatively high tensile strength of the paper, but relatively low caliper (lower bulk) at a given basis weight. By contrast, at the other extreme, a completely unrefined fiber will have a greater tendency to regain its three-dimensional character even after such processes as wet pressing [5,6]. Ordinarily, such unrefined fiber would have poor interfiber bonding ability due to having a low relative bonded area with adjacent fibers in a sheet [18]. Part B of Fig. 1 shows the proposed system in which NFC, after having been treated with cationic starch, preferentially becomes attached to the surfaces of the negatively charged fiber surfaces, thus providing a highly bondable layer. It is proposed that the combined system with NFC pretreated with cationic starch can provide synergistic benefits of added strength, beyond what would be achieved by either NFC or cationic starch alone. At the same time it is proposed that a bulkier sheet structure can be achieved.

The hypothesis just introduced offers a potential way to achieve paper strength at lower apparent density, at least before calendering, but there still is a need to address concerns regarding the rate of water removal during sheet formation. Past studies have shown that the presence of highly fibrillated cellulose in papermaking furnish has the potential to greatly slow the drainage rates [10,13]—and potentially decrease production rates—on a paper machine. To address this concern, the present research considers two approaches. First, the fact that the NFC becomes treated with a cationic polymer makes it more likely that the NFC will become attached to fiber surfaces; it follows that such bound NFC would not have as much of an adverse effect on dewatering in comparison with unattached fine cellulosic matter [19]. Further, the addition of a suitable dosage of colloidal silica to a mixture of NFC and cationic starch may be able to increase the dewatering rates without interfering with the system's ability to contribute to paper strength. The effect of the silica additive on dewatering has been well demonstrated [20–22], but not in the case of NFC that has been treated by cationic starch, then treated by colloidal silica, then added to papermaking furnish. While the use of cellulosic micro- and nanofibrillated materials have been associated with being very costly, our group recently has conducted the most extensive manufacturing cost analysis for MNFC, determining values as low as US$1200 per dry ton equivalent of MNFC. This means that a 1% MNFC charge would cost approximately US$12 per finished ton of paper [23] in addition to the cost of the cationic polymer additive. This application cost should be compensated by savings in energy cost (related to refining) and potentially fiber reduction.

Figure 2 provides a schematic view of how the proposed system might be later optimized, depending on the process and product requirements of a given paper mill. Key variables in control of the papermaking team would include the degree



2. Schematic view of the proposed process, in which the level of refining of the main fiber furnish is dialed back, and NFC is pretreated with either a high-charge polymer (just to make it cationic) or with cationic starch (in an effort to achieve a synergistic strengthening effect), followed by optional colloidal silica treatment (either to the treated NFC or to the whole furnish) for tuning of drainage and water retention value effects.

of refining of the main furnish, the amount and refining level of highly fibrillated cellulose (NFC in the present research), the amount of cationic starch or other cationic polymer used to treat the highly fibrillated cellulose, and the amount and addition point of an optional drainage-promoting additive such as colloidal silica. As shown, there are two purposes for the addition of cationic starch. One is to contribute bonding strength to the paper structure. The other is to hold the NFC effectively on the fiber surfaces in the course of the process described in the figure.

Because the present work was designed to evaluate a concept, the conditions selected do not necessarily correspond to a specific grade of paper. Meaningful characterization of the apparent density of the material was a main concern in the present work; therefore, an intentionally high basis weight condition was selected. Preliminary work showed that good formation uniformity could be achieved and pressing operations could be carried out effectively with a basis weight of 350 g/m^2. By working at a very high basis weight, the effect of differences in surface smoothness, relative to the evaluation of density, is greatly reduced. The selection of bleached hardwood kraft as the major furnish type was based on the widespread use of hardwood fibers in some bulky grades of paper, such as book paper and tissue, as well as the excellent formation uniformity that can be achieved in handsheet evaluations. It made sense to include some softwood fiber as well because papermakers often employ a blend to achieve tear strength objectives and efficient paper machine operations.

EXPERIMENTAL

Chemicals and materials

A mixture of 70% bleached hardwood kraft pulp and 30% bleached softwood kraft pulp (southern U.S. fibers) was either unrefined or corefined using a laboratory Hollander beater to the following CSF levels: 514 mL (unrefined), 473 mL (lightly refined), and 283 mL (heavily refined). The NFC, of the spray-dried form (lot no. U38, grade cellulose nanofibrils [CNF]), was provided by the University of Maine, Process Development Center. Properties of the NFC material have been presented [24]. Tap water was added to achieve a solids content of 0.5%, and sodium sulfate was added to reach an electrical conductivity of 1000 µS/cm at room temperature (approximately 22°C [71.6°F]) before further testing. Sodium bicarbonate was added at the 1.0 mM level as a means of achieving approximately neutral pH.

The cationic starch used in this work was Chargemaster L340 (Grain Processing Corp.; Muscatine, IA, USA), a cationic starch paste of the pregelatinized type. It was prepared for use by dilution in water at least 1 h before usage. The colloidal silica was NP 320 (Kemira; Helsinki, Finland). This product is known to be of the gel type; it consists of irregular fused chains of approximately 2 nm primary silica particles and is designed to promote both fine-particle retention and increased rates of dewatering when used in combination with a high-mass, low-charge cationic polymer such as cationic starch. The no. 40,901-4 poly-diallyldimethylammonium chloride (poly-DADMAC) (Sigma-Aldrich; St. Louis, MO, USA) is a

linear homopolymer with one positive (quaternary nitrogen) charge per repeat unit with a molecular mass range 100000–200000 g/mol).

Pretreatments and blending

Pretreatments of the NFC were carried out at 1000 µS/cm electrical conductivity. The cationic starch solution (diluted to 1% solids solution before addition) was added with agitation, to achieve the selected addition level (10% or 50% starch solids on the basis of NFC solids). The colloidal silica was added, after addition of cationic starch to NFC, at levels of either 5%, 10%, or 20% on the basis of NFC solids. Solids were adjusted so that the overall percentage solids were constant during experimentation.

Sheet forming, pressing, and drying

To enable reliable evaluation of caliper and apparent density, the sheets were prepared with a high basis weight. On the basis of preliminary tests, a basis weight of 350 g/m² was selected. Sheets were prepared using a procedure that was otherwise consistent with TAPPI Standard Test Method T 205 "Forming handsheets for physical tests of pulp". As described, a roller was used to initially press the damp sheets. Each sheet was subsequently passed through the nip of an Atlas laboratory wringer at the automated feed rate (2.8 cm/s) and an applied load equivalent to 50 lb (22.68 kg) applied to a 12-in. (30.48 cm) wide nip between 2-in. (5.08 cm) diameter rubber rollers, giving a nip load of 0.742 kg/cm. Sheets were dried under restraint, using the standard TAPPI rings to hold the circular sheets. Sheets were equilibrated to TAPPI test conditions (50% RH, 23°C [73.4°F]) TAPPI T 402 "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products" at least overnight before physical testing.

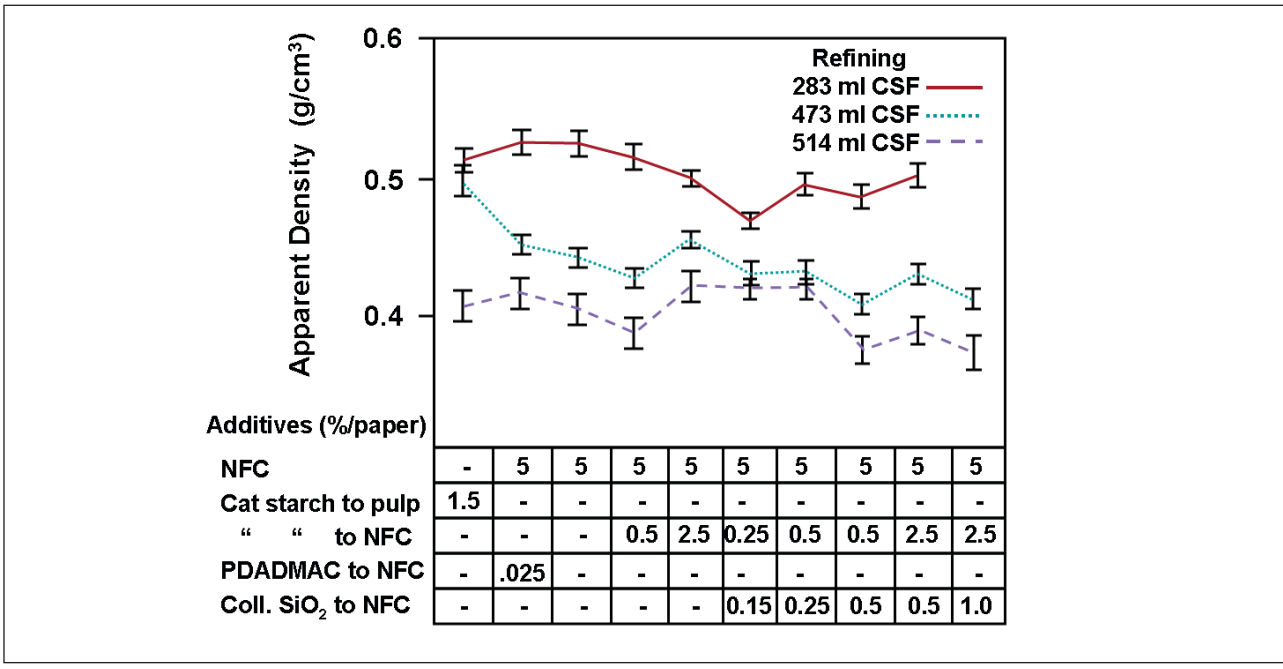
Process-related tests

Dewatering rate tests were carried out using a modified Schopper-Riegler method [25]. Briefly stated, 1000 mL of 0.5% solids suspension, prepared in just the same way as for the other experiments, was placed in the device above a closed sealing ring. A stopwatch was started simultaneously with the opening up of the ring to permit drainage, and the mass of filtrate was evaluated with a tared pan balance after passage of 20 s.

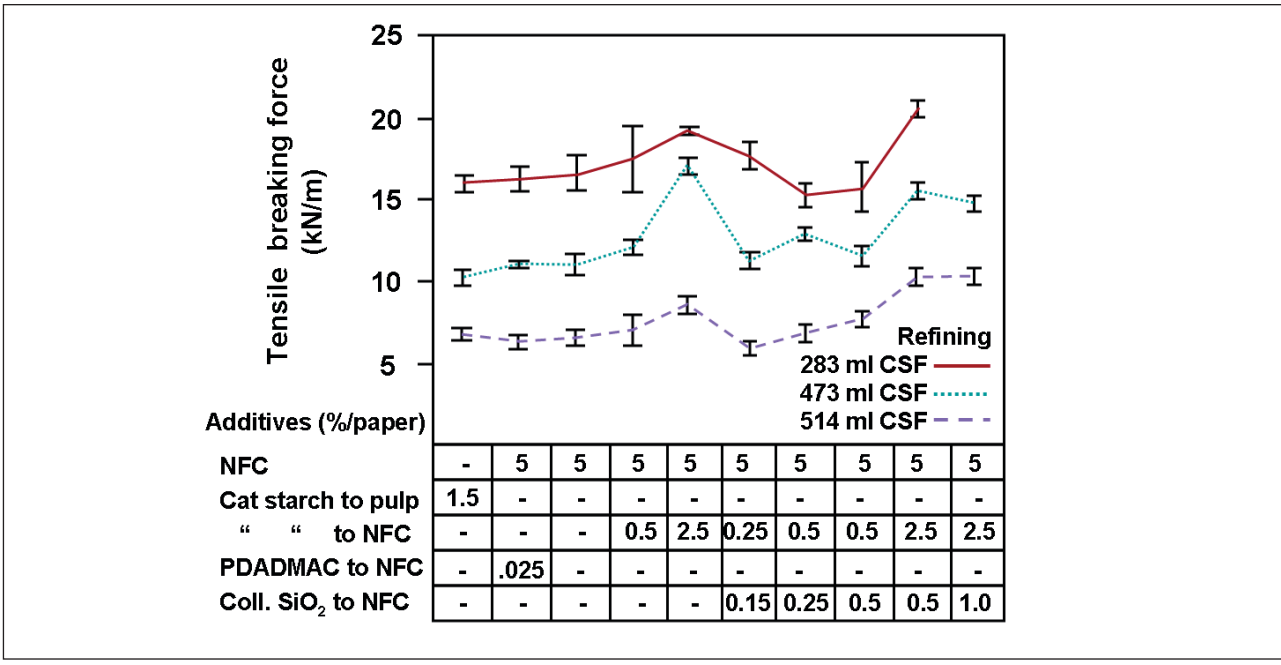
Streaming potential values were obtained using a simple apparatus consisting of a Buchner funnel fitted with a 200-mesh stainless steel screen having two welding-wire probes, one in contact with the aqueous phase on each side of the screen. The difference in voltage readings when applying either about 90 kPa or zero differential pressure across the pad of fibers (using house vacuum) was recorded for each test. The sensing unit of the device was the same as what is described in [26], except that the pressure difference was applied by vacuum rather than by compression and the device was operated manually.

Physical tests

Caliper tests were conducted according to TAPPI T 411 "Thickness (caliper of paper, paperboard, and combined board)". Tensile strength was based on TAPPI T 494 om-96 "Tensile



3. Effects of refining level of the main furnish, as well as effects of nanofibrillated cellulose (NFC), cationic (Cat) starch, and colloidal silica (Coll. SiO_2) treatments on the apparent density of the pressed handsheets. Error bars give 95% confidence intervals for the mean values. See Experimental section for further explanation of the conditions. (PDADMAC = polydiallyldimethylammonium chloride.)



Additives (%/paper)										
NFC	-	5	5	5	5	5	5	5	5	5
Cat starch to pulp	1.5	-	-	-	-	-	-	-	-	-
" " to NFC	-	-	-	0.5	2.5	0.25	0.5	0.5	2.5	2.5
PDADMAC to NFC	-	.025	-	-	-	-	-	-	-	-
Coll. SiO_2 to NFC	-	-	-	-	-	0.15	0.25	0.5	0.5	1.0

4. Tensile breaking force of the pressed handsheets as a function of refining level of the main furnish, as well as effects of nanofibrillated cellulose (NFC), cationic (Cat) starch, and colloidal silica (Coll. SiO_2) treatments. Error bars give 95% confidence intervals for the mean values. (PDADMAC = polydiallyldimethylammonium chloride.)

properties of paper and paperboard (using constant rate of elongation apparatus)". Taber stiffness was measured using TAPPI T 489 om-04 "Bending resistance (stiffness) of paper and paperboard (Taber-type tester in basic configuration)". The weight corresponded to "+1000 stiffness units" and the degrees were 15 on each side. Gurley densometer (Gurley Precision Instruments; Troy, NY, USA) values (resistance to air permeation) were evaluated as in TAPPI T 460 om-96 "Air resistance of paper (Gurley method)".

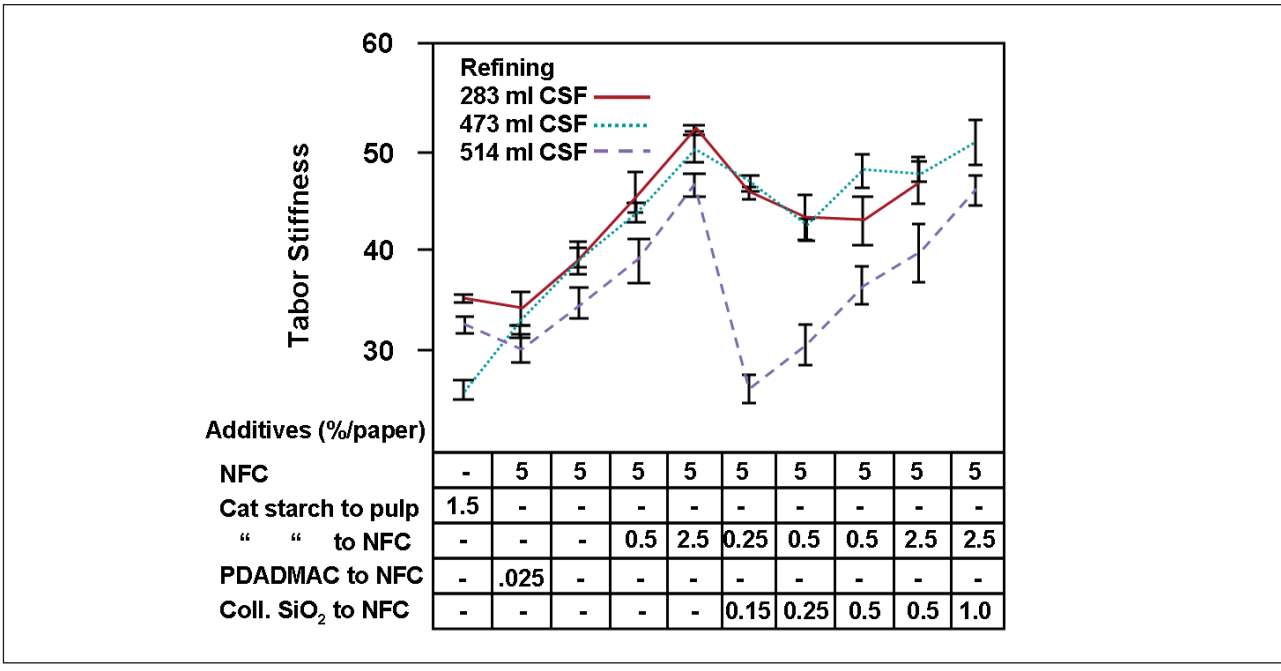
RESULTS

Apparent density

As shown in **Fig. 3**, the extent of refining of the main kraft furnish had a major effect on the apparent density of the resulting handsheets. Note that the first column of data corresponds to a system in which there was no NFC, and instead a relatively high level of cationic starch was added for purposes of strength enhancement. The labels of the other columns correspond to conditions as described in the Experimental section. Results of preliminary tests showed that in the absence of cationic polymer, the added NFC did not significantly increase the strength of the resulting sheets; therefore the third column titled "Default" can be regarded as a reference point that would not be very different from the main furnish with no additives of any kind. This finding is consistent with the observations of Campano et al. [27], who showed that some kind of retention additive may be needed to achieve important benefits of NFC addition. The label "Fixative" means that the high-charge cationic polymer was employed as a means of electrostatically attracting the NFC to fiber surfaces in the absence of the cationic starch dry-strength additive. The remaining columns correspond to different treatment levels of cationic starch (the first additive) and colloidal silica (the second additive). The highly refined pulp yielded the densest sheets, and the unrefined fibers yielded the lowest-density sheets. The most interesting finding was that the apparent density achieved with the lightly refined pulp was strongly dependent on the addition of NFC, as well as its pretreatment. The presence of NFC tended to yield less-dense paper in comparison with the blank that had no NFC. These results are tentatively attributed to the highly flexible nature of NFC, which might allow greater recovery of caliper of the paper sheet after the press nip while still maintaining interfiber bonding.

Paper strength

Figure 4 gives corresponding results for paper tensile strength. As would be expected [17], tensile strength generally increased as a function of increasing level of refining. However, significantly increased tensile strength was also achieved when adding NFC (at the 5% level) that had been treated by a high level of cationic starch (equivalent to 2.5% addition on a product basis). The increase was especially notable in the case of the lightly refined pulp. Also of note, greatly increased strength was achieved when NFC had been treated not only with a high level of cationic starch, but also with colloidal silica. These results suggest that NFC that has been pretreated with a high level of cationic starch, either with or without subsequent treatment with colloidal silica, can achieve substantially increased strength. In particular, the strength levels as-



5. Taber stiffness of the pressed handsheets as a function of refining level of the main furnish, as well as effects of nanofibrillated cellulose (NFC), cationic (Cat) starch, and colloidal silica (Coll. SiO_2) treatments. Error bars give 95% confidence intervals for the mean values. (PDADMAC = polydiallyldimethylammonium chloride.)

sociated with the high level of refining could be approached by adding the pretreated NFC to the lightly refined pulp. The results achieved when adding the cationic starch–pretreated NFC (with a high starch level of 2.5% on the basis of sheet solids) greatly exceeded the results achieved when adding either NFC by itself or when adding a high level of cationic starch (1.5% by mass) separately in the absence of NFC. Though the levels of starch were different (1.5% versus 2.5% on the basis of sheet solids) in this comparison, it is well known that cationic starch tends to reach a point of diminishing returns when it is added at high levels to ordinary papermaking furnish [28]. A wide range of positive effects on tensile strength have been reported when highly fibrillated cellulose has been added to papermaking furnish, of which the following reports are representative [7,8,13,14,27,29]. The diversity of results from the various studies can be rationalized on the basis of different properties and refining of the main fibers, unknown efficiencies of retention of the highly fibrillated cellulose in most reported cases, and the inclusion or exclusion of polymers contributing to bonding or fiber agglomeration.

Figure 5 shows corresponding results for Taber stiffness. As shown, although NFC by itself could increase paper stiffness, much greater increases were achieved when using NFC that had been pretreated by increasing levels of cationic starch. Remarkably, the stiffness of sheets prepared with lightly refined fibers with cationic starch-pretreated NFC were in the same range of stiffness (e.g., sometimes higher, sometimes lower) compared with those prepared without NFC and a high level of cationic starch at the high level of refining of the main furnish (281 mL CSF) (first set of data at the left of the plot). Another aspect worth noting is that high levels of stiffness were achieved whether or not colloidal silica had been added after the cationic starch.

Paper air permeability and smoothness

Gurley densometer tests revealed that the level of refining of the main furnish was the most important factor governing air permeability. The readings were generally in the ranges shown in **Table I**, regardless of the addition of NFC, cationic starch, or colloidal silica in different combinations. Pretreatment with high levels of cationic starch, especially when followed by colloidal silica, increased the resistance to air permeation, but such effects were minor in comparison with that of the level of refining of the main kraft fibers.

Other investigators who have evaluated effects of adding highly fibrillated cellulose (micro- or nanofibrillated cellulose) to fiber slurries before paper formation have reported increases in Gurley densometer and related test values in the range of 16%–460% [7,8,10,15,27,29,30]. A possible explanation for the different behavior in the present work, where no significant effect of NFC on air permeability was found, is that the pretreatment system allowed the NFC to deposit efficiently onto the surfaces of the main fibers in the paper rather than occluding pores within the paper and thus impeding dewatering [31]. Of course, such a hypothesis would need to be evaluated in future work.

Tests carried out with a Parker Print Surf apparatus showed only minor differences in smoothness among the samples, regardless of refining level of the main furnish and treatments with cationic starch.

Refining Level	Gurley Densometer Value, s/100 cm³	Parker Print Surf Roughness, µm
Unrefined	3.4–5.3	10.2–10.4
Lightly refined	7.3–10.8	10.3–11.1
Heavily refined	21.1–29.9	11.5

I. Gurley densometer results for the 350 g/m² sheets.

Results of process-related tests

Table II shows the results of tests to evaluate the dewatering rate and the zeta potential for certain test conditions that were selected on the basis of their strongly contrasting effects relative to paper strength. As shown in the table, the treatment of the NFC with a high level of cationic starch (2.5% cationic starch solids on the basis of the mass of solids in the paper) resulted in an apparent increase in the mean value of filtrate that had drained within 20 s in the modified Schopper-Reigler test device; however the change was not significant at a 95% confidence level. Greater increases in dewatering rate were obtained in two cases where the cationic starch treatment of NFC was followed by colloidal silica. Both such treatments yielded significant increases in dewatering rate relative to treatment of the NFC with starch alone. Such findings are consistent with the reported effects of sequential treatment with cationic starch and colloidal silica, when this is done under ordinary papermaking conditions [21]. However, this is the first time such an effect has been reported when the additives were used to pretreat NFC.

Although freeness tests are widely used as a means to assess the drainability, and hence the refining levels of pulps, such results do not necessarily correlate with drainage rates observed on paper machines. In particular, as shown by Gess [32], filtration tests with high basis weight sheets—which is essentially the situation employed during standard freeness tests—tend to exagerate the effects of furnish conditions such as the level of fines on the rate of dewatering. Thus, it would be reasonable in future work to confirm the present findings with pilot-scale or commercial-scale forming equipment.

Results of zeta-potential tests, based on the streaming potential method [26], showed that the treated stock suspension had a negative zeta potential for all of the conditions considered. Of note, the addition of colloidal silica, which has a negative surface charge, resulted in less negative values of zeta potential. This change is tentatively attributed to a greater adsorption of the cationic starch onto cellulose surfaces in the presence of colloidal silica [33].

DISCUSSION

The processing sequence considered in this work, which may substantially decrease the need to refine papermaking fibers, has the potential to extend the life cycle of pulp resources. Though it is well known that fibers from recovered paper can be used multiple times in new paper products, excessive mechanical refining of a fiber, in the course of multiple cycles of usage, is to be avoided. By applying most of the refining energy to a minor component of the cellulose, which becomes microfibrillated or nanofibrillated, the degree of mechanical degradation of the main fibers can, in principle, be minimized.

While the strategy described in this work shows promise in terms of reducing the refining of the main furnish, achieving lower apparent density, and maintaining key strength properties, it is important to keep in mind that some other properties will not match those of paper made under the default conditions with higher levels of refining. The paper will tend to be rougher and more porous. In some paper grades, where surface smoothness or porosity are critical, this might be a deal breaker. In other cases the resulting surface either may be suitable relative to the target performance of the paper, or it might be overcome by subsequent processing steps (e.g., calendering or coating). Whether a production

Condition*	3 Default	5 High Starch	9 with Silicon Dioxide	10 with Silicon Dioxide
NFC level, %	5	5	5	5
Cationic starch to NFC, % based on paper mass	0	2.5	2.5	2.5
Colloidal SiO_2 to NFC, % based on paper mass	0	0	0.5	1
Filtrate mass after 20 s, g				
Mean	511.5	530.4	552.1	583.3
Upper 95% Confidence limit	532.0	545.7	559.0	597.4
Lower 95% Confidence limit	491.0	515.2	545.2	569.1
Mean zeta potential, mV	-92	-93	-62	-55

NFC = nanofibrillated cellulose; SiO_2 = silicon dioxide.
* Conditions correspond to the third, fifth, ninth, and 10th columns of data in Figs. 3, 4, and 5.

II. Drainage rate and zeta potential of selected stock suspensions.

scheme as outlined in this study can achieve lower wet-web solids after the wet presses, while still providing lower apparent density, will need to be established through experiments that simulate realistic production speeds for modern paper machines and a variety of fiber types. If the answer is yes, then pretreatment of NFC with cationic starch (and optional colloidal silica), together with reductions in the refining level of the main furnish, has the potential to save energy because there will be less water to evaporate from the paper web after the wet presses. A further question that needs to be addressed in subsequent work is the extent to which the apparent advantages, especially in terms of stiffness and apparent density, might be obscured in cases where calendering (to achieve a smoothenss target) is a necessary part of the production scheme.

It needs to be emphasized that certain process options cosidered in this work showed much lower benefits. In particular, as has been noted in a review of earlier work [27], addition of cationic starch directly to papermaking furnish usually can provide only modest gains in paper's strength. Likewise, just adding NFC to the furnish did not achieve important gains in dry strength. Rather, the results of this work suggest a synergistic effect when cationic starch and highly fibrillated cellulose are used in combination. One way to view this synergism is that the NFC may be acting as an extender for the cationic starch, allowing the dry strength agent to form bonds between surfaces that could not be spanned by individual starch molecules. Seen another way, the cationic starch may be providing a mechanism of retention, as well as enhanced hydrogen bonding ability, to the NFC. In either case, the treated NFC holds promise as a papermaking wet-end additive, and it merits further research.

While the results shown in this study demonstrate some interesting points, many questions remain to be considered. For example, the present work does not shed any light on whether the pretreatment of NFC can contribute meaningful benefits in the case of paper grades that require relatively high values of apparent density. In such cases it might be hypothesized that interfiber joints comprising NFC might prove to be structurally inferior to what can be achieved by more direct bonding between long fibers within the paper structure. Another limitation is that the present work considered only one type of NFC, ignoring whether similar benefits can be achieved when using coarser, more easily obtained materials, such as fibrillar cellulosic fines [34] or microfibrillated cellulose [35]. Also, there are many more optional sequences in which the chemical additives can be combined—for instance, adding the colloidal silica to the combined furnish rather than as part of the pretreatment of the NFC. Finally, different basis weights and furnish types can be considered, possibly at the pilot papermaking scale, to establish the findings under more realistic conditions for certain paper and paperboard grades.

It was proposed that a sharp decrease in refining of papermaking fibers can be expected to result in reduced moisture in the wet web after pressing, while at the same time yielding lower apparent density of the resulting sheet. Only the last part of this hypothesis has been evaluated and shown to be valid by the present work; indeed, the strategy of using unrefined or less-refined fibers, together with an NFC-based bonding strategy, yielded low apparent density at favorable levels of tensile strength and stiffness. There has been little published research regarding the effects of wet-end parameters relative to the dewatering effectiveness of wet pressing [36], and there is a need for follow-up in that area for the present work. There are theoretical reasons, however, to support an assumption that increased refining will tend to inhibit release of water during wet pressing. According to Zhao and Kerekes [37], the main resistance to compression of the paper web in a wet-press nip is always hydrostatic in nature. It follows that resistance to compression will be dominated by factors that block the passage of water (i.e., the ability of highly conformable and high-surface area matter to act as hydraulic seals, as well as water retention within the fiber cell wall) [31]. By contrast, the cell walls of the fibers themselves are always much too weak, if the lumen is not filled with water, to make a major contribution to avoiding compressing within the wet-press nip [37]. Research is being planned to address such questions under conditions of interest for grades of paper.

CONCLUSIONS

Tests carried out in the laboratory support a new strategy for achieving lower apparent density in paper products, while maintaining tensile strength, stiffness, and rates of dewatering during the formation of paper. Such goals can be achieved by decreased refining of the main fiber furnish, which ordinarily would result in a sharp decrease in strength attributes of the paper. Addition of either untreated NFC or cationic starch were relatively ineffective in boosting the strength of the paper made from the under-refined fibers. But by pretreating the nanocellulose with high levels of cationic starch, the resulting paper strength was comparable to what ordinarily would have been achieved at a higher level of refining. Though NFC is known to be unfavorable for the rates of drainage from papermaking furnish, test results showed that such issues can be addressed in a new way—pretreatment of nanocellulose first with cationic starch, then with colloidal silica before addition to the main pulp suspension. Bulkier paper, prepared by use of the described strategy, can be expected to save materials and energy when producing certain paper grades, such as return postcard stock, some grades of boxboard, book paper, and paper towels. **TJ**

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LITERATURE CITED

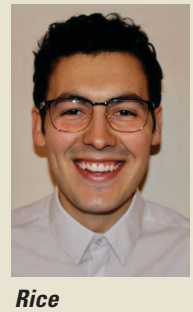
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ABOUT THE AUTHORS

We chose to undertake this research because we had a promising idea and wanted to test it. We had never actually tried such an approach with reduced refining levels, cationic starch, and silicon dioxide.

To address the difficult aspects of this research, we had to try different settings of the wet-press device to establish a procedure. We were surprised to learn that only a combination of both nanocelluse and cationic starch was effective.

An interesting finding was that colloidal silica made it possible to improve drainage, while still getting a big strength gain. Mills that make low-density products want to achieve higher caliper, or use recycled fiber can benefit from this work. The next step is to investigate other grade applications, such as dense grades.



Rice



Pal



Gonzalez



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