CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECT OF NFC FROM ORGANOSOLV CORN STALK PULP ON RETENTION AND DRAINAGE DURING PAPERMAKING

ANA BALEA, NOEMÍ MERAYO, MARÍA SEARA, ELENA FUENTE,
ANGELES BLANCO and CARLOS NEGRO

Department of Chemical Engineering, Complutense University of Madrid,
Avda Complutense s/n, 28040 Madrid, Spain
✉ *Corresponding author: Angeles Blanco, ablanco@ucm.es*

Valuable chemical compounds can be produced from corn stalk in a biorefinery by means of the organosolv process. However, 41% of the corn stalk is cellulose, which is commonly used to produce bioethanol whose profitability is not high because of the cost of the process. The use of this cellulose to produce nanofibrillated cellulose (NFC) could improve the profitability of the process. NFC has gained increasing interest as reinforcing additive in paper and composite materials, such as films, food packaging, emulsifiers and nanofilters. The objective of this research has been to study the effect of NFC, obtained from organosolv corn stalk pulp, on retention and drainage processes and its interaction with retention aids when NFC is used to reinforce recycled paper. Results showed that a low NFC dose (0.5 wt%) was required to increase by 20% the tensile index of paper, but it decreased the drainage rate. However, this effect could be overcome with the studied retention aids.

Keywords: nanofibrillated cellulose, recycled paper, retention, drainage, mechanical properties

INTRODUCTION

In recent years, there has been an increasing interest in the search for renewable and sustainable alternatives that might replace petroleum as a source of chemicals, materials and energy. The production of liquid fuels and industrial chemicals from biomass will rely most heavily on the utilization of polysaccharide, lignocellulosic and triacylglyceride feedstocks. These materials are available, easily assembled and storable in large quantities. In addition, these materials may be converted into products that are identical, or functionally equivalent, to current petroleum-based liquid fuels and industrial chemicals.[1]

In this scenario, the valorization of lignocellulosic biomass, particularly agricultural and forestry residues, can be performed by converting their components jointly through combustion, pyrolysis, gasification or liquefaction, or separately. Nowadays, this last valorization method has led to the development of the biorefining concept. Therefore, lignocellulosic biorefining technologies include a primary separation of its main constituents, cellulose, hemicelluloses and lignin, as well as a further treatment and processing to obtain different platform chemicals to design consistently structured compounds as chemical building blocks. The economic competitiveness of the obtained products is highly dependent on the separation and purification technologies used and the process energetic efficiency. For this proposal, process simulation tools are very useful to design a competitive and effective biorefinery scheme.[2-6]

Many methods have been developed for pretreating lignocellulosic feedstocks,[7-8] the organosolv method being appropriate for higher lignin containing materials.[9] Although the organosolv pretreatment is more expensive at present than the leading pretreatment processes,[10-12] the interest towards the organosolv process has increased due to its potential within the biorefinery concept, allowing an integral use of the raw material obtaining high added value by-products.[13]

Organosolv fractionation of lignocelluloses has a long history, the earliest study applying organic solvents to treat lignocellulosic material dates back to 1893, when Klason[14-15] used ethanol and hydrochloric acid to separate wood into its components to study the structure of lignin and carbohydrates. Subsequently, a wide variety of

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other organic solvents, e.g., various alcohols, phenol, acetone, propionic acid, dioxane, various amines, esters, formaldehyde, chloroethanol, whether pure or in aqueous solutions, and in the presence or absence of acids, bases or salts as catalysts, were used to extract lignin, increasing the cellulosic fraction digestibility. Its suitability has been investigated for several woody and non-woody biomasses and it proved effective for hemicelluloses/lignin degradation and cellulose crystallinity reduction.[16-17]

The future development of the organosolv pretreatment should focus on the integrated utilization of biomass components and the decrease of the pretreatment costs. This can be achieved by reducing the amount of organic liquid used in the pretreatment, increasing the added value of the by-products, and optimizing the whole process and some other aspects related to the reduction of energy and chemicals consumption.[13] Some recent new developments in the organosolv process have been proposed, including an ultrasonic-assisted organosolv/liquid oxidative pretreatment for the simultaneous recovery of cellulose, bioethanol and biochemicals from oil palm fronds;[18] new organosolv biomass fractionation process (Clean Fractionation), which achieves an average yield of cellulose fraction recovery of 47.7% w/w,[3] and the LignoFibre (LGF) organosolv process for production of high-quality biomass components based on the use of phosphinic acid.[19]

Recently, the cellulose obtained from biorefining has come to be used for the production of nanocellulose.[20-22] Nanofibrillated cellulose (NFC) is receiving great attention due to its applicability in a variety of domains, its renewable nature, high availability and complete biodegradability.[23]Among these applications, NFC has received increasing interest as strength additive in paper production due to its high specific surface area, improving the bonding degree and paper strength.[24-25]

Most studies produce NFC from wood pulp and apply it to virgin pulp, and very few are focused on recycled paper despite its poor mechanical properties caused by the decrease of recovered paper quality.[26-27] Furthermore, there is a lack of studies about the effect of NFC on retention and drainage and on the interaction of NFC with retention aids, since most studies use cationic starch to retain NFC,[24] which is not a common retention aid in recycled paper production. In industrial applications, the strong water retention of NFC may deteriorate the production efficiency of the paper machine, thus it is important to find a correlation between drainage characteristics and strength enhancement to facilitate optimized use of this very promising biomaterial.

In this research, the main objective was to assess the effect of NFC, obtained from organosolv corn stalk pulp from agricultural residues, first to increase the strength of recycled paper formed from old newspapers (ONP) and old magazines (OMG) and, second to investigate its effect on the behavior and efficiency of different flocculants commonly used in papermaking, studying retention and drainage processes.

EXPERIMENTAL

NFC production

NFC was obtained from never dried corn stalk organosolv pulp refined at 5000 rpm in a PFI mill to reach a CSF of 170 mL and a Kappa index of 16.8. This pulp was obtained by the organosolv cooking process and it was not bleached in order to minimize the required treatment and its environmental impact. The experimental organosolv conditions used were defined as follows: solvent concentration of ethanol–water: 40/60 w/w; temperature: 165 °C; reaction time: 60 min; liquid/solid ratio: 6:1.

NFC was obtained by TEMPO mediated oxidation, by using 15 mmol of NaClO per each gram of pulp. The oxidation conditions applied were those described by Saito *et al.*[28] The pulp obtained with the organosolv process still contains many compounds different form cellulose as shown by the Kappa index and the percentage of non-cooked compounds reaches 5.4 wt%. These compounds react with the NaClO and reduce the oxidation of cellulose during the TEMPO process according to previous researches.[29]

Once the pulp was oxidized, a cleaning process was performed through filtration steps using distilled water to reach a pH value around 7. Finally, six steps of homogenization at 600 bar were applied to the pulp in a laboratory homogenizer PANDA PLUS 2000 manufactured by GEA Niro Soavy (Parma, Italy).

NFC characterization

NFC was characterized by atomic force microscopy (AFM) in the National Centre of Electronic Microscopy at the Complutense University of Madrid, by using an AFM Nanoscope III A multimode (Bruker) with scanners of 1 µm and 15 µm and with a FESP probe oscillating at 86.5 kHz. To prepare the NFC sample for AFM, a drop of diluted NFC suspension (0.3-0.5 wt%) was extended and dried on mica substrate at 40 °C.

The amount of carboxylate groups of the oxidized fibers was determined by conductometric titration of the pulp after TEMPO treatment. Oxidized pulp was cleaned to remove the TEMPO aid and all the by-products of the TEMPO reaction, before the conductometric titration. Then, 5 mL of 0.01 M NaCl was added to the pulp sample, which contained 0.15 g of dry matter, and the pH of the pulp was adjusted to 2.5-2.8 by adding 0.1M HCl to protonate all the carboxylate groups. MQ water was added to the sample to reach a total volume of 55 mL. 0.05 M NaOH was added to the sample in consecutive additions of 0.2 mL, while the sample was continuously stirred. The conductivity of the sample was recorded after each addition. The amount of carboxylic groups was calculated from the amount of NaOH consumed in their neutralization, which was determined from the curve of conductivity *vs* the amount (meq) of NaOH added, following the method developed by Habibi *et al.*[30]

The cationic demand (CD) of the NFC suspensions was obtained by colloidal titration of the diluted suspensions between 0.05-0.1 wt%, with 0.001 N polyDADMAC, by using a particle charge detector, Mütek PCD04, manufactured by BTG Instruments GmbH (Herrsching, Germany).

The transmittance of the NFC suspensions diluted at 0.1 wt% was measured in the wavelength interval of 400 to 800 nm by using a Cary 50Conc UV-Visible spectrophotometer manufactured by Varian Australia PTI LTD.

The polymerization degree (PD) was calculated from the limiting viscosity number (intrinsic viscosity) of the NFC suspensions, which was determined by following the international standard ISO5351/1 with cupriethylendiamine as solvent. The method was based on the Mark-Houwink-Sakurada equation and values given by Henrikson *et al.*[31] were used in this study. The yield in NFC was also determined; a diluted NFC suspension (0.1 wt%) was centrifuged at 5000 rpm for 30 min in order to isolate the nanofibrillated fraction contained in the supernatant from the non-fibrillated or partially fibrillated one retained in the sediment fraction. The supernatant was recovered, weighed and oven-dried at 105 ºC until constant weight.

Retention aids

Three different retention aids were selected for this study: (1) CS, which improves the mechanical properties of recycled paper and is a natural polymer well-known in the paper industry; (2) the dual system formed by coagulant and cationic PAM, selected because it is a synthetic polymer commonly used in recycled paper mills; and (3) a new polymer of PVA to test its efficiency related to the other known aids.

Pulp and sheet preparation and characterization

Pulps were prepared through disintegration of 20 g of dry recovered paper of a mixture formed by 60% ONP: 40% OMG, by using a Messmer pulp disintegrator (Mavis Engineering Ltd, London) at 180000 revolutions and 1.0 wt% consistency. The recovered paper with the correspondent amount of NFC was left to soak for at least 24 h before disintegration to favour the swelling of fibers. Once the pulp was disintegrated, it was mixed with the correspondent retention aid: cationic starch (CS), the dual system of coagulant and cationic polyacrylamide (PAM) and polyvinylamine (PVA).

The pulp was used to prepare handsheets with basis weight of 60 g/m^2 in a normalized (ISO 5269/2, DIN 54 358) sheet former Rapid-Köthen from PTI (Vorchdorf, Austria). These handsheets were conditioned in a weather chamber at 25 ºC and 50% humidity for 24 h before physical and mechanical tests were performed by using an AUTOLINE 300 from Lorentzen & Wettre (Stockholm, Sweden).

Retention and drainage measurements

The drainage time of the pulp suspensions was measured with a Dynamic drainage analyser (DDA) equipment from Pulpeye (Örnsköldsvik, Sweden), which provides the related drainage time of a pulp applying vacuum, as well as the total solids retention from the cake. Experiments were performed with 300 mL of pulp at 0.5 wt% consistency. The initial vacuum level of the DDA was 0.30 bar and a 76 μm (200 mesh) stainless steel wire cloth was used.

After 30 s of initial stirring at 300 rpm, the retention aids were added to the pulp in the DDA (for the dual system, PAM was added after 60 s of coagulant addition). After another 30 s of mixing, the stirring was stopped and drainage began by opening a pneumatic piston and applying vacuum.

RESULTS AND DISCUSSION

Evaluation of NFC properties

Fig. 1 shows that the diameter of most of the NFC obtained was between 4 and 6 nm, and no aggregates of fibrils are observed. Therefore, the suspension is disaggregated on elementary fibrils. For the TEMPO-oxidised fibres, the amount of carboxylic groups obtained was 0.52 mmol/g. The cationic demand for CD was 0.198 meq/g and the intrinsic viscosity indicated a PD of 541. The transmittance at 400 nm and 800 nm was 89.9% and 95%, respectively. The yield of NFC was 86%, which indicates that it contains around 14% of non- or partially fibrillated materials, which can be separated by centrifugation.

Effect of retention aids on both drainage and mechanical properties

Several doses of each retention aid were selected and tested based on some previous experimentation and recommendations of the suppliers. As one of the main objectives of adding NFC to the pulp is to increase the tensile index, this parameter was measured along with the drainage time and the solid retention (Figures 2 and 3). Whereas PAM and PVA strongly decreased the drainage time, CS was not an effective aid for the pulp, because it slightly increased the drainage time (Fig. 2). All the retention aids tried on the pulp without NFC improved the solids retention, which was the maximum with 0.25 mg/g of PAM, 5 mg/g of CS or 7.5 mg/g of PVA, (around 89.5%). However, while CS increased the tensile index of the sheets (around 10% increase), PAM and PVA decreased this property. A stronger negative was that of PAM, reaching around 30% reduction in tensile index, while the decrease with the maximum addition of PVA was of about 15% (Figure 3).

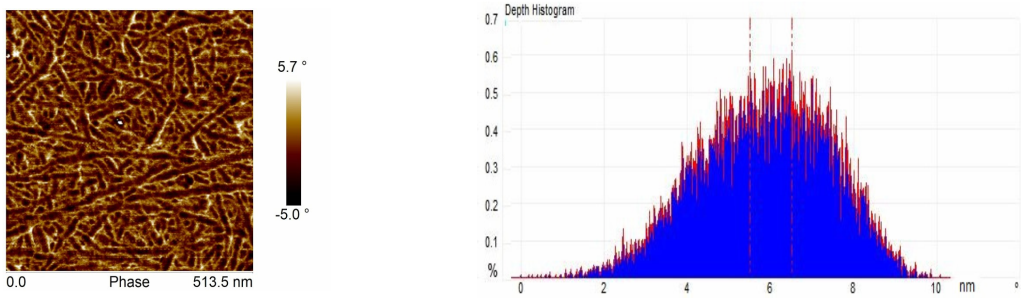

Figure 1: AFM image (500 nm X 500 nm) and depth distribution of NFC obtained from corn stalk organosolv process

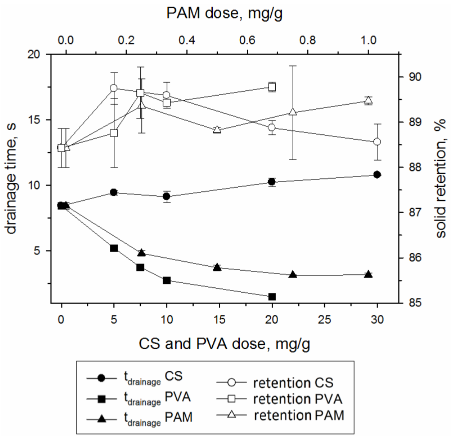

Figure 2: Effect of retention aids on drainage time and solids retention without NFC addition

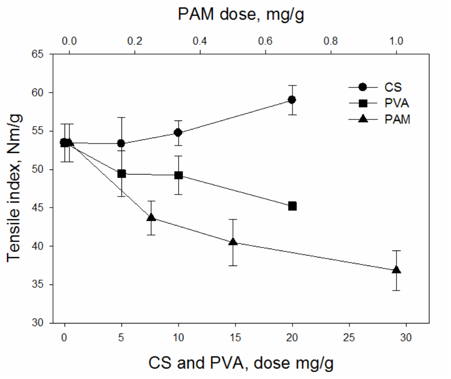

Figure 3: Effect of retention aids on tensile index without NFC addition

Therefore, the retention aids under study had contrary effects on drainage time and tensile index. As a result, it was necessary to select the optimum dose, taking into account that as the drainage time improves, the tensile index gets worse, and vice versa.

Optimization of the retention systems in presence of NFC

Once the effect of the retention aids on the drainage time and the tensile index was known, the effect of the NFC concentration on the drainage process was studied. As the NFC concentration increased, the drainage time also notably increased (Figure 4), and the solid retention slightly decreased (Figures 5 and 6) before the addition of any retention aid.

Although, in the absence of NFC, CS did not improve drainage (Figure 4), unexpectedly the presence of NFC changed the effect of CS, especially when 1.5 and 3 wt% NFC were added to the recycled pulp. In these cases, a dose of CS notably decreased the drainage time. However, further increase of the CS dose beyond 10 mg/g increased the drainage time, as it happened with lower NFC concentrations (Figure 4a). Consequently, at low NFC concentrations, CS was not efficient as a drainage aid; however, there is an increase in the efficiency of this aid at doses of NFC of 1.5 wt% or higher, in which a careful selection of the CS dose is necessary.

In the cases of the addition of PVA and PAM, the efficiency of both as drainage aids increased with the NFC concentration. NFC retention in flocks improved drainage notably, and it was possible to reach similar drainage times to those obtained in the absence of NFC, if the right dose of PAM or PVA was used.

For example, when 1.5 wt% NFC was used, a dose of 10 mg PVA per gram of dry pulp decreased the drainage time to a similar value to that for pulp without NFC (Figure 4b). When applying 3 wt% NFC, 10 mg/g of PVA is still the optimum value to achieve a significant decrease in the drainage time. In the case of PAM, smaller doses were required (Figure 4c) and 0.25 mg/g was enough to remove the effect of NFC (0.5 wt%) on drainage, and to increase the retention up to 90% (Figure 5). The minimum drainage time was reached with 0.75 mg/g of PAM (Figures 5 and 6). Higher doses did not achieve further decrease in drainage time.

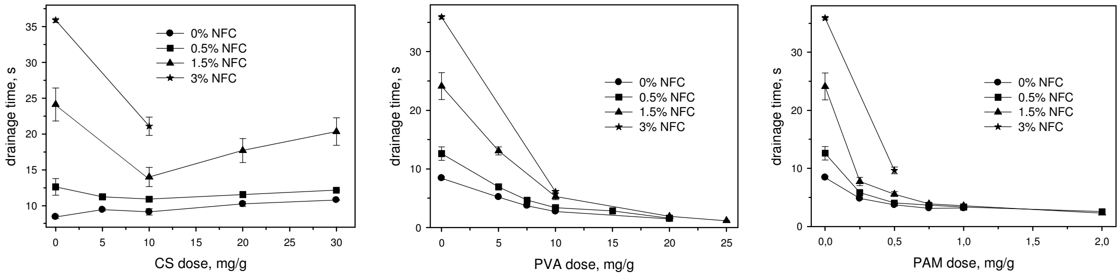

Figure 4: Drainage time evolution with a dose of retention aids: a) CS, b) PVA and c) PAM, depending on NFC concentration

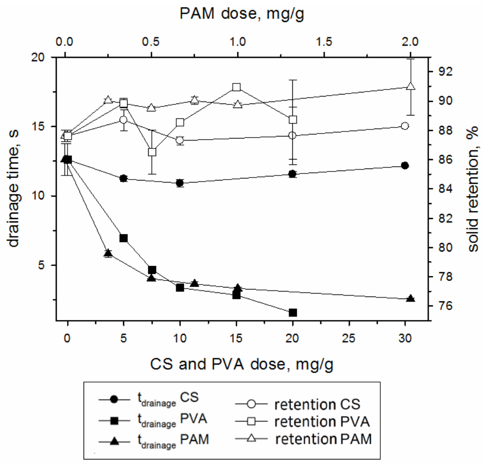

Figure 5: Effect of retention aid dose on drainage time and solid retention with 0.5% NFC dose

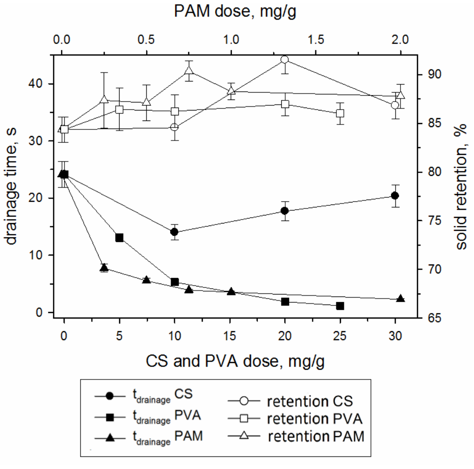

Figure 6: Effect of retention aid dose on drainage time and solid retention with 1.5% NFC dose

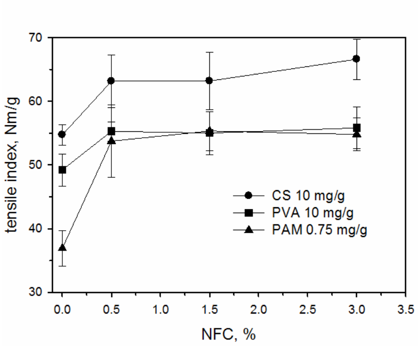

Figure 7: Effect of NFC on tensile index using the optimum dose of retention aids

In any case, despite the large differences in drainage time depending on the NFC concentration before the addition of retention aids, an appropriate dose of PVA or PAM can improve the drainage, obtaining similar drainage time values regardless of the NFC concentration.

Effect of NFC dose on the mechanical properties

Paper sheets were prepared from the pulp containing different NFC concentrations and the optimal dose of each retention aid (Figure 7). The main objective, in this case, was to assess the influence of the NFC dose on some properties of recycled paper depending on the retention aid used, without the addition of any other strength agent in the process. The use of the retention aids affected the tensile index of the recycled paper without NFC, but in different ways. Whereas CS slightly increased the tensile index of the paper sheet, PVA decreased it and PAM strongly decreased this property. Therefore, the reference value of the tensile index was significantly different depending on the retention aid considered. The lowest amount of NFC tried (0.5 wt%) was high enough to cause a significant increase of the tensile index being the optimal dose regardless of the retention aid used (Figure 7). A higher amount of NFC did not achieve further increase in tensile index. The addition of 0.5 wt% NFC to the pulp removed the negative effect of PAM and PVA on the sheet strength, by increasing the tensile index up to a value similar to that of pulp without aids. The maximum increase in tensile index was achieved in the presence of PAM, around 45%, followed by CS and PVA with around 15 and 12%, respectively.

Furthermore, the combination of NFC with CS (10 mg/g) allowed reaching the highest value of the tensile index, but with an increase in drainage time, whereas PVA and PAM strongly decreased drainage time, recovering the tensile index with NFC addition. A future study can be performed using the optimum dose of NFC to reduce the dose of PVA and PAM needed.

CONCLUSION

The results obtained from this research show that the appropriate combination between NFC and drainage and retention aid is a key for the use of NFC in the recycled paper production. This combination offers at least two possibilities:

(1) To neutralize the negative effect of the retention aids on the tensile strength, maximizing the machine productivity. The optimal dose of a highly efficient retention aid (0.75 mg/g of PAM or 10 mg/g of PVA) can be used to maximize the drainage rate and retention without decreasing the tensile strength of the sheet if 0.5 wt% of the pulp is replaced by NFC.

(2) To maximize product strength, the combination of 10 mg/g of CS with a replacement of the 0.5 wt% of pulp by NFC allows to obtain a product with a superior tensile index (15% higher) but at the expense of reducing machine productivity (drainage time increases by 29%).

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