

Accepted Manuscript

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PII: S0144-8617(17)30590-8
DOI: <http://dx.doi.org/doi:10.1016/j.carbpol.2017.05.073>
Reference: CARP 12359

To appear in:

Received date: 28-3-2017
Revised date: 11-5-2017
Accepted date: 24-5-2017

Please cite this article as: Campano, Cristina., Miranda, Ruben., Merayo, Noemi., Negro, Carlos., & Blanco, Angeles., Direct production of Cellulose Nanocrystals from old newspapers and recycled newsprints. *Carbohydrate Polymers* <http://dx.doi.org/10.1016/j.carbpol.2017.05.073>

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Direct production of Cellulose Nanocrystals from old newspapers and recycled newsprints

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Highlights

- Viability of the direct production of CNC from recycled papers was proved.
- Similar CNC can be obtained but with different yields and purities.
- Two-step pretreatment favors purity of CNC but reduces process yield.
- Similar crystallinities and aspect ratios of all CNC were observed.

ABSTRACT

Cellulose nanocrystals (CNC) are high added value products which can be used in many applications. In this research, CNC were directly produced from two recycled papers: old newspapers (ONP) and 100% recycled newsprint (NP). CNC were also obtained from NP by previously isolating the cellulose particles by alkali and bleaching treatments. CNC yield and quality was assessed through lignin and ash determination, X-ray diffraction analysis, atomic force microscopy and thermogravimetric analysis. Not only crystallinities resulted similar (92-95%), but also aspect ratios (L/d) (each in the range of 50-120). However, different CNC purities and hydrolysis and process yields were

obtained. Thus, CNC purity decreased from 93 to 77%, hydrolysis yield was reduced from 64 to 58% but process yield strongly improved from 35 to 60% when no pretreatment was used. Therefore, this study proves the viability of the direct production of CNC from recycled papers.

Keywords: Cellulose nanocrystals, newsprint, recycled paper, process yield, alkali and bleaching pretreatments, old newspaper.

1. INTRODUCTION

Cellulose, the most abundant renewable and naturally occurring polymer, has been used for nearly 150 years either as raw fibers or after some modifications. Cellulose consists of linear bonds of glucose as monosaccharide ($C_6H_{10}O_5$)_n, conforming both crystalline and amorphous regions (Mohamed, Salleh, Jaafar, Asri & Ismail, 2015). Last can be removed by acid hydrolysis, remaining the crystalline part, which is known CNC, with a rod-like morphology (Habibi, Lucia & Rojas, 2010).

In the last decades, the paper has become one of the most recycled products with a recycling rate of 71.5% in Europe (CEPI 2015). However, paper industry is suffering an important crisis. In last years, while the demand of packaging papers is increasing continuously, the use of newsprint and some other graphic papers is decreasing. For example the production of packaging papers in Europe increased 7.2% in the last five years, while newsprint production decreased in 28.3% (CEPI 2015). This fact supposes huge challenges for the newsprint mills in order to maintain their competitiveness. As a consequence some companies have shut down production lines and others are looking for other market niches by developing new products and high added value products (Delgado-Aguilar, Tarres, Pelach, Mutje & Fullana-i-Palmer, 2015). In this sense, the on-site production of nanocellulose can be a very promising alternative.

CNC are growing in popularity since their first isolation by Ranby in 1951, through a sulfuric acid hydrolysis of cellulose fibers (Ranby, 1951). These CNC exhibit many advantages compared to cellulose fibers, such as high strength, high surface area, unique optical properties, lightweight, stiffness, etc. Not only their properties and wide

application prospects have attracted a high interest, but also their inherent renewability and sustainability (Habibi, 2014).

CNC can be prepared from any single source containing cellulose, such as wood pulps (Du et al., 2016; Hu et al., 2014), plant sources such as ramie or cotton (Csiszar, Kalic, Kobol& Ferreira, 2016; Peresin, Habibi, Zoppe, Pawlak& Rojas, 2010), food byproducts or wastes such as rice straw or rice husk (Lu& Hsieh, 2012; Martínez-Sanz, Vicente, Gontard, Lopez-Rubio& Lagaron, 2015) or bacterial cellulose (Campano, Balea, Blanco& Negro, 2016). To the best knowledge of the authors, only two recent references have studied the technical feasibility of using recycled paper as raw material to produce CNC (Danial et al., 2015; Mohamed et al., 2015). This cellulose source presents some advantages compared to wood pulps, such as the high availability and the low cost.

CNC production from recycled paper has been made after isolation of cellulose fibers by using intensive treatments. On the one side, Danial et al. (2015) boiled ONP for more than 12 h for two times, treating the resulting pulp with 5% (w/v) NaOH and followed by 2% (v/v) NaClO treatment. On the other side, Mohamed et al. (2015) used wastepaper, but they removed the printed areas of ONP, thus really using non-printed newsprint (NP). They applied an alkali treatment with 5 wt% NaOH at 125°C for 2 h followed by a bleaching treatment with 2% (w/v) NaClO₂ at 125°C for other 2 h, repeating this step until a white pulp was obtained. In addition, the used newsprint seems to be free of fillers, which is not the most typical case. In Europe, for example, ~98% of newsprint is produced from recovered paper and filler loadings are usually in the 15-20% range.

This work aims to determine the technical feasibility of producing CNC directly from recycled papers (ONP and NP) with fillers and without a previous isolation of cellulose fibers. To compare, a two-step pretreatment similar to the antecedents in the literature, based on an alkali treatment and a bleaching step has been applied to NP (NP-B). Thus, the effect of the presence of impurities in sample before hydrolysis on the quality of CNC has been assessed.

2. EXPERIMENTAL

2.1 Materials

ONP with an ISO brightness of 45% and 14.5 wt% ash content and NP with an ISO brightness of 56% and 14.0 wt% ash content were used as raw materials. Microcrystalline

cellulose (MCC), Avicel, was used as reference of pure cellulosic material, supplied by Sigma-Aldrich. Chemicals used for acid hydrolysis and alkali treatment, H_2SO_4 and NaOH, were supplied by Sigma Aldrich (analytical reagent grade) and used without further modification. Furthermore, NaClO used for bleaching as a 10% w/v solution (technical grade), was supplied by Panreac.

2.2 Methods

Different quality CNC were prepared:

- ONP: direct acid hydrolysis.
- NP: direct acid hydrolysis.
- NP-B: Two-step pretreatment (alkali and bleaching treatments, similar to antecedents on literature) to NP, followed by acid hydrolysis. The purpose is to assess the effect of pretreatment on CNC properties.
- MCC: direct acid hydrolysis. These CNC were prepared to compare the effect of the raw material on CNC properties.

Two-step pretreatment. Alkali and bleaching treatments were applied to NP resulting in NP-B, adapting the procedure of Mohamed et al. (2015). Briefly, NP was disintegrated for 30 min at 3000 rpm, using a Messmer pulp disintegrator (Mavis Engineering Ltd, London, UK). Then, it was treated with 5 wt% NaOH for 2 hours at 125 °C. After that, pulp was washed with distilled water. Then, 2% (w/v) NaClO was added and left to interact for 2 hours at 125 °C. After, it was subsequently washed with distilled water to reach constant pH. NP-B pulp was dried overnight at 105 °C and then it was milled through an IKA analysis grinder A10 (IKA-Werke GmbH, Staufen, Germany).

CNC production. After milling ONP, NP, NP-B and MCC, acid hydrolysis of dry milled samples was carried out with 60 wt% H_2SO_4 at 45 °C. This acid concentration was selected based on the study of Chen et al. (2015) in which the yield is maximized while minimizing conversion of CNC to sugars. The ratio between acid and extracted cellulose was set at 13.5 mL/g and the reaction time was 90 min based on preliminary tests. First, 200 mL of prepared H_2SO_4 solution were slowly added during 2 min to avoid overheating of dry milled sample. Then, it was agitated in glass beaker on a thermostatic bath with an impeller covered by Teflon at 500 rpm. After the reaction time, mixture was diluted 10 times with distilled water to stop the reaction and left to settle overnight. The sediment was washed four times by centrifugation using a 3-16L centrifuge (JP Selecta S.A,

Barcelona, Spain) at 4500 g for 15 min to remove excess of acid. Finally, the suspension was dialyzed against distilled water using tubing membranes made of regenerated cellulose with a molecular weight cut-off of 12000-14000 Da (Medicell International Ltd, London, UK), until neutral pH was reached. All experiments were carried out by triplicate.

2.3 CNC characterization

CNC purity. After acid hydrolysis and dialysis, different proportion of ash and lignin can be present together with CNC. The amount of mineral fillers in the different CNC was measured through ash content at 525°C following ISO 1762. Lignin content was measured indirectly by Kappa number according to Tappi 236 om-99 using the following equation: $Lignin (\%) = 0.13 \cdot Kappa\ number$ (Tasman& Berzins, 1957). The remaining percentage up to 100% corresponds to the value of CNC purity.

Crystallinity index (CrI) and average crystalline dimension (ACD). X-ray diffraction (XRD) spectra was obtained using a Philips X'Pert MPD X-Ray diffractometer with an autodivergent slit fitted with a graphite monochromator using Cu-K α radiation operated at 45 kV and 40 mA. XRD patterns were recorded from 3 to 80° at a scanning speed of 1.5 °/min. Crystallinity index (Cr.I) was determined using Segal's method (Segal, Creely, Martin& Conrad, 1959) by the eq. (1).

$$Cr.I(\%) = \frac{I_{002} - I_{am}}{I_{002}} \cdot 100 \quad (1)$$

Where I_{002} is the intensity of the 002 plane at $2\theta = 22.5^\circ$ and I_{am} is the intensity of the amorphous scatter at $2\theta = 18^\circ$.

ACD was determined by the widely-used Scherrer eq. (2).

$$ACD = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (2)$$

Where ACD is the perpendicular size to the diffracting plane represented by the maximum peak, K is a dimensionless shape factor (normally 0.9), λ is the wavelength of the radiation in the diffraction experiment ($\lambda = 0.15406$ nm), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is its diffraction angle also in radians (French& Cintron, 2013).

Polymerization degree (PD). PD was determined from intrinsic viscosity (η), by the following equation: $\eta = 0.42 \cdot PD$ valid for $PD < 950$ (Henriksson, Berglund, Isaksson,

Lindstrom& Nishino, 2008). η was measured by the method of dissolving cellulose in cupri-ethylene-diamine (CED) solution, according to ISO 5351.

Morphology. Surface morphology and size distribution were determined using Atomic Force Microscopy (AFM) with an AFM multimode Nanoscope III A (Bruker), in tapping mode. A drop of a solution of 0.05% of consistency was deposited on a clean mica surface and left to dry overnight at room temperature before analysis.

Thermogravimetric analysis (TGA). Thermal stability was assessed using a Seiko Exstar 6000 TGA/DTA thermobalance, measuring the sample weight from 30 to 1000 °C at a heating rate of 10 °C/min with an air flow of 30 mL/min.

2.4 Process yields

Hydrolysis yield. Hydrolysis yield was calculated by eq. (3).

$$\text{Hydrolysis yield (\%)} = \frac{m_{\text{CNC}}}{m_{\text{before hydr.}}} \cdot 100 \quad (3)$$

Where m_{CNC} is the dry mass of the produced CNC (with the remaining impurities) and $m_{\text{before hydr.}}$ is the dry mass of sample before hydrolysis.

Process yield. CNC or process yield was determined by the ratio of m_{CNC} and the initial dry mass before pretreatment ($m_{\text{before pret.}}$) (eq. (4)).

$$\text{Process yield (\%)} = \frac{m_{\text{CNC}}}{m_{\text{before pret.}}} \cdot 100 \quad (4)$$

Pretreatment losses. This percentage mainly includes the amount of lignin, hemicellulose and mineral fillers removed during the pretreatment, although the loss of some cellulose fibers is also possible. The mass loss during pretreatment was determined through the eq. (5).

$$\text{Pretreatment losses (\%)} = \frac{m_{\text{before pret.}} - m_{\text{before hydr.}}}{m_{\text{before pret.}}} \cdot 100 \quad (5)$$

Hydrolysis mass loss. The mass loss during hydrolysis was determined by the sum of two values: dissolved amorphous cellulose and losses during hydrolysis. Dissolved amorphous cellulose (DAC) was determined through chemical oxygen demand (COD) of the filtrated supernatant after hydrolysis. Nanocolor® COD 1500 test method (Macherey-Nagel GmbH) and a Thermo Aquamate UV-Vis spectrophotometer were used to obtain the COD value. Assuming that all present organic materials correspond to cellulose, DAC can be calculated from the following equation: $\text{DAC}(\text{mg/L}) = \text{COD}/1.185 = 2877.6 \cdot$

I^{600} obtained by Q. Q. Wang et al. (2012) through calibration with MCC. To be consistent with the rest of the calculations, a percentage value has been determined (eq. (6)).

$$DAC (\%) = \frac{DAC(mg/L) \cdot V_{total}(L)}{m_{before\ pret.}(mg)} \cdot 100 \quad (6)$$

Where V_{total} is the total volume when hydrolysis mixture is diluted 10 times.

Hydrolysis losses were determined through the remaining amount until 100%, mainly composed of dissolved $CaCO_3$ and cellulose loss. Eq. (7) shows the formula used to calculate this value.

$$Hydrolysis\ losses (\%) = 100 - Process\ yield - Pret.\ losses - DAC \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 CNC purity

Since raw materials of this study are not pure cellulose, their main components, cellulose+hemicellulose, lignin and ash were determined, both before and after hydrolysis (Figure 1).

The most used mineral fillers in papermaking are kaolin and calcium carbonate, while others such as talc or titanium dioxide can be used in a lower extent (Lourenco, Gamelas& Ferreira, 2014). As expected, the initial ash content of ONP and NP is almost the same, around 14%. However, after the two-step pretreatment, it is reduced to around 12%. The main cause is the loss of these mineral fillers in the filtration step after each treatment.

During acid hydrolysis, not only amorphous cellulose is dissolved but also $CaCO_3$ (soluble at acid pH). Therefore, ash contents in CNC samples are reduced to 11.5, 11.9 and 5.7%, for CNC-ONP, CNC-NP and CNC-NP-B, respectively. Presence of fillers is also verified through XRD analyses (showed in Section 3.2), where kaolinite and $CaCO_3$ are identified in the raw materials, while kaolinite is the only mineral filler present in CNC samples.

Lignin is present in most recycled papers, including ONP and NP. Lignin is removed from the pulp for producing papers with high optical properties, but only partially for newsprint, which must be produced as economically as possible. Results show that the amount of lignin in NP is lower than in ONP (6.5% vs. 9.1% Figure 1a) because of its partial removal during recycling. However, differently to bleached chemical pulps, where lignin is virtually removed, mechanical or deinking pulps used for newsprint production

can still present a high amount of lignin. Bleaching of NP (NP-B) reduced the lignin content to 2%.

During acid hydrolysis, lignin fractionates into an acid insoluble and acid soluble fractions. Due to dissolution of amorphous cellulose, percentage of lignin referred to the total amount of CNC in CNC-ONP and CNC-NP increased from 9.1 to 12.5% and from 6.5 to 10.2%, respectively. However, when CNC are produced from NP-B, lignin content is reduced due to the solubilization of acid soluble lignin is higher than dissolution of amorphous cellulose. In this case, only a residual amount of 0.9% is present. In case of repeating the bleaching process a second time, the percentage of lignin would be almost zero. It occurs with CNC-MCC, in which raw material is pure cellulose. However, the acid insoluble lignin remained after hydrolysis approximately in the same amount.

From Figure 1b, it is clearly observed how a better quality in sample before hydrolysis produced a higher CNC purity. This value is similar in CNC-ONP, and CNC-NP (76.0% and 77.8%, respectively). However, this percentage not only includes cellulose but also hemicellulose since both ONP and NP have typically a cellulose/hemicellulose ratio between 1 and 2.2 (Sun& Cheng, 2002). Because of hemicellulose removal during alkali pretreatment, dissolution of lignin during bleaching and calcium carbonate during acid hydrolysis, CNC-NP-B purity increased up to 93.3%, considered as the percentage of cellulose. Depending on the final application of these CNC, CNC purity has to be taken into account.

The amount of lignin has a direct impact in color, which could limit their application when high optical properties are required. Figure 2 shows physical appearance of dry sample before hydrolysis and the obtained CNC dispersions. The black color of CNC-ONP corresponds to remaining inks used in newspapers printing, mainly black, which masked color of other components. In the case of NP and CNC-NP, a brown color indicates the presence of lignin in the sample. As it has been previously explained, percentage of lignin in this sample (10.2 %) is much higher than 0.9% corresponding to CNC-NP-B. However, a lighter color but still beige has been obtained instead of white obtained for CNC-MCC, probably due to the presence of a residual amount of lignin.

3.2 Crystallinity and average crystalline dimension (ACD)

Typical crystalline cellulose associated peaks are obtained in MCC spectra $2\theta = 15-17^\circ$, 22.5° and 35° (Figure 3a), confirming its high degree of crystallinity in a cellulose I

structure (Xu et al., 2013). Peak at around 29.5° in raw materials is due to the presence of CaCO_3 , which is the most intense peak of its XRD spectra. As it is soluble in acid media, it is not detected in CNC samples (Figure 3b). There are also observed peaks at 12.5° and 25° in both raw materials and CNC, which are attributed to kaolinite. In CNC these peaks are more intense due to the increase of its relative amount in CNC samples by removal of amorphous parts of cellulose and CaCO_3 .

Initial Cr.I value for ONP (85.9%) and NP (86.5%) are in accordance with Mohamed et al. (2015). They used non-printed areas of ONP, i.e. NP and obtained 82.0% of Cr.I. An increment in Cr.I is obtained when NP is bleached (NP-B), due to partial removal of hemicellulose and lignin (Sheltami, Abdullah, Ahmad, Dufresne & Kargarzadeh, 2012), reaching 90.6% of Cr.I.

After hydrolysis, Cr.I increases in all cases as expected. CNC-ONP show lower value of Cr.I than CNC-NP (92.6% and 93.4%, respectively), mainly due to the slightly lower hydrolysis yield. In addition, according to Donnet (1993), typical used inks are oxidized in acid media, thus consuming some amount of H_2SO_4 . Therefore, less amorphous cellulose is removed from raw materials, reaching a lower Cr.I. The subsequent acid hydrolysis of NP-B is favored by purity, reaching a value of Cr.I of 94.8%, very close to that of CNC-MCC (95.5%). However, the increase in Cr.I was not the same in all cases, those being 6.7, 7 and 4.2 percentage units for CNC-ONP, CNC-NP and CNC-NP-B, respectively. In case of CNC-MCC, the degree of Cr.I improvement is lower (3.9 percentage units) since the maximum value has been reached near that of raw material (91.6%) (Dufresne, 2012). These values are in accordance with Danial et al. (2015), whose CrI increased 10.1 percentage units after hydrolysis using ONP as raw material. However, as pretreatments of Mohamed et al. (2015) were much more aggressive, increment in CrI after acid hydrolysis is much lower, only 1.7 percentage units.

It is supposed that higher ACD of cellulose is observed when purity is higher due to the narrowing of the crystallite size distribution (Lu & Hsieh, 2012). Therefore, ACD values increase with purity, being 7.5, 10.3 and 12 nm for ONP, NP and NP-B and 32.5, 41.2 and 45 nm for their respective CNC. In all cases, ACD increases with acid hydrolysis treatment, due to that higher removal of amorphous cellulose favors aggregation of CNC. These values also checked the higher efficiency of the CNC production process when purer is the sample before hydrolysis.

3.3 Polymerization degree (PD)

It is well known PD of cellulose decreases rapidly when acid hydrolysis takes place, until the so-called level-off PD (LOPD) is reached, which depends on the cellulose origin. A higher LOPD confers better strength properties when CNC are applied to different matrixes (Habibi et al., 2010).

ONP and NP had different PD, being 640 and 550, respectively (Figure 4). The reason could be related with the number of recycling cycles and ageing as explained by Čabalová, Kačík, Geffertand Kačíková (2011). Including a pretreatment, polymer length and therefore PD is reduced from 551 to 400 (Figure 4), mainly caused by the action of chemicals. However, CNC obtained from ONP, NP and NP-B present similar PD: 182, 181 and 194, respectively. The main reason for this behavior can be that LOPD might have been reached. On the other side, when MCC is used to prepare CNC, PD is not affected (225), thus acid hydrolysis only triggered a reduction in diameter, not in length.

These results are in accordance with Hamad and Hu (2010), who got a PD value of 100 for CNC produced from a commercial softwood kraft pulp, and with Zhang, Lu, Chen and Lv (2012) who obtained 174 from bamboo fibers.

3.4 Morphology and size distribution

CNC obtained from ONP present a high degree of aggregation as it is shown in Figure 5. Presence of inks or lignin can be cause this behavior, being difficult to distinguish in AFM images if a single or CNC aggregates are observed. However, CNC obtained from NP and NP-B show better dispersion and thinner appearance due to removal of some impurities. On the contrary, due to the high purity of CNC-MCC, they also tend to aggregate, but in this case, hydrogen bonding seems to be the cause, what makes CNC size very difficult to determine.

As being composed of lower amount of lignin, production of CNC from NP-B is more effective than ONP and NP, thus more surface area in the CNC was obtained. In terms of size, CNC-ONP have 2.94 ± 0.99 nm wide and 371.18 ± 74.15 nm long (Aspect ratio (L/D) between 50 and 200), while CNC-NP are found to be 3.26 ± 2.90 nm wide and 218.22 ± 48.64 nm long (L/D ratio between 50 and 90). As it is deduced from a

representative image of CNC-ONP (Figure 5a), it is difficult to give a correct length due to the high agglomeration. CNC-NP-B dimensions were 4.40 ± 3.91 nm wide and 356.27 ± 137.28 nm long (L/D ratio between 50 and 120). The reason why length of CNC-NP-B is much higher than that of CNC-NP could be the aggregation between CNC individuals. These values are similar to those reported for CNC isolated from NP by Mohamed et al. (2015), where they had 5.78 ± 2.14 nm wide and 121.42 ± 32.51 nm long (aspect ratio of 5-40), and from ONP by Danial et al. (2015), who reached an average value of ~ 4 nm wide and ~ 170 nm long (average aspect ratio of 42). A higher aspect ratio is achieved in all CNC produced in this study compared to those in the literature. When these CNC are applied to reinforce different matrixes, a higher aspect ratio can suppose a higher increment in strength.

3.5 Thermogravimetric analysis

TG/DTG studies were carried out to compare thermal stability of the different samples. Samples before hydrolysis present an endothermic peak at around 350°C where most of sample is loss (Figure 6a and 6c). However, acid hydrolysis triggers a separation of this sample decomposition in two steps: the first at 200°C and the second at 370°C (Figure 6 b and d). After this temperature, a lower but continuous mass loss occurred in TG curves of CNC, remaining a significant residue still after 1000°C .

The initial weight loss between $100\text{-}130^{\circ}\text{C}$ of all samples was assigned to evaporation of residual water and volatile matter in samples (Sheltami et al., 2012). Peak at around 750°C of ONP and NP DTG curves (Figure 6c) was identified as CaCO_3 (Sanders & Gallagher, 2002), confirming that it is only present in raw materials but not in CNC.

Lignin has shown to be difficult to decompose in nitrogen atmosphere. However, in air atmosphere it usually decompose between 430 and 540°C (Canetti, Bertini, De Chirico & Audisio, 2006). Therefore, when lignin is removed through pretreatments, maximum decomposition peak moved to lower temperatures, from 352°C for ONP and NP to 316°C for NP-B (Figure 6c).

All CNC samples started an earlier degradation than raw materials mainly caused by deposition of sulfate groups during H_2SO_4 hydrolysis, thus triggering a dehydration reaction (N. Wang, Ding & Cheng, 2007). However, despite ONP and NP TGs are quite similar, their behavior after acid hydrolysis is different. While first DTG peak of ONP is about 220°C at a decomposition rate of around -12% /min, that of NP is almost 30°C lower

(around 190°C) and mass loss rate is around third (-4%/min). Since the main difference between these two raw materials is ink content, it has been assumed that this impurity has caused this behavior. Typical used inks in newsprint industries are based on mineral oils (Biedermann & Grob, 2010), which can react with sulfuric acid changing the decomposition profile.

When lignin and hemicelluloses are removed from NP and CNC are produced, first maximum degradation temperature ($T_{\max 1}$) increases from 190 to 209°C (due to hemicelluloses removal) and second peak temperature ($T_{\max 2}$) decreases almost 60°C (from 367 to 307°C) because of lignin removal. The results obtained for CNC-NP-B are in accordance with Mohamed et al. (2015), obtaining almost the same TG/DTG curves.

Residues at 600°C were analyzed to compare with existing literature. These residues were different in ONP (30.0%) compared to NP (26.0%), because of their different inherent composition. As during two-step pretreatment hemicellulose and lignin are removed, but ash content is very similar, residue at 600°C of NP-B increases up to 32.1%. It has been demonstrated that sulfate groups introduced at the surface of CNC act as flame retardant as well as reduce thermal stability (Roman & Winter, 2004). For that reason, residue at 600°C increases after acid hydrolysis treatment. This value for CNC-NP-B is exactly the same as that obtained by Mohamed et al. (2015) (31.3%), who used a similar procedure and the same raw material (NP). It is quite similar to that of CNC-MCC (31.3 and 29.5%, respectively), what indicates their similar composition, only differing in ash content: 5.7% compared to 0.1%, respectively.

3.6 Process yields

Since ONP and NP composition is similar, hydrolysis yields resulted in close values, 60.8 and 58.4%, respectively (Figure 7a). However, with the inclusion of the two-step pretreatment, this yield increased up to 64.3%. The main reason is the removal of impurities during pretreatment, favoring the access of acid to cellulose. In addition, as MCC is purely a crystalline cellulose material, hydrolysis yield is considerably higher (75%). In comparison with bibliographic values, hydrolysis yield of 60.8% for CNC-NP is slightly higher than that obtained by Mohamed et al. (2015) (54.6%), who obtained CNC from NP. In addition, it has been demonstrated that lower quality materials can be used to prepare CNC with a hydrolysis yield comparable to that obtained by Q. Q. Wang et al. (2012), who used a bleached Kraft eucalyptus pulp and obtained a value of 58.7 %.

As it has been observed in other CNC properties, slight differences have been found between ONP and NP process yields, varying between 58.4 and 60.8%, respectively (Figure 7b). Nevertheless, a better quality raw material (MCC) improved the process yield from 60.8 to 75%. The main reason is the cellulose purity of different raw materials, so that when it is pure (MCC), process yield is considered the theoretical maximum according to Chen et al. (2015), who ensure that it is possible to reach a process yield of more than 70% from a bleached eucalyptus pulp. In CNC-NP-B, process yield decreased to 34.6% due to removal not only of impurities, but also the loss of cellulose or other compounds during pretreatments. Nevertheless, this yield is almost double to that obtained by Danial et al. (2015), who use ONP as raw material to produce CNC of similar quality to CNC-NP-B and obtained a process yield of ca. 19%. Mohamed et al. (2015) used NP, but pretreatment losses were not considered in the process yield (they only calculated hydrolysis yield), thus no comparisons can be done.

DAC values are higher when quality of raw material is lower, thus meaning that more amorphous cellulose is present in its structure. As shown in Figure 7b, 26.8% of NP was amorphous cellulose, being almost the same amount to that of ONP (26.7%) but more than twice as MCC (11.7%). Pretreatment losses value includes removed lignin, hemicellulose, some mineral fillers and cellulose loss during two-step pretreatment. Mohamed et al. (2015) reduced hemicellulose content from 15.33% to 0.28% and lignin amount from 29.46 to 0.89% by using a similar pretreatment. The sum of these two percentages is 44.79%, which makes the 46.2% obtained in the present study, a reasonable percentage for pretreatment losses of NP-B.

3.7 Comparison of results

CNC produced directly from ONP and NP present similar properties (Table 1). The main differences are based on the presence of inks in ONP, which entails a residuary black color in CNC-ONP.

However, there is an increment in CNC quality when the two-step pretreatment is included in the process. Briefly, CNC-NP-B present higher purity (93.3 compared to 77.8%), Cr.I (94.8 compared to 93.4%), PD (194 and 181), aspect ratio (50-120 compared to 50-90, respectively) and hydrolysis yield (64.3 compared to 60.8%) than CNC-NP.

Although CNC-ONP have lower quality than the other CNCs of this study due to the higher levels of inks and lignin, their production cost is much lower and the process yield

higher than other approaches to produce CNCs. First, the raw material is cheaper (around 100 €/ton) and the cost of chemicals for alkaline and bleaching treatments are saved. Furthermore, as the removal of impurities is not carried out before hydrolysis, process yield is also higher. This is a very interesting approach to obtain “low-cost” CNCs which can be used in certain applications where the quality requirements are not so high, i.e. for paper and board production.

CNC-NP are produced from a better quality raw material, with no inks and a lower content on lignin, but its cost is also higher (around 500 €/ton). However, as direct production of CNC was used, costs related to pretreatments are still saved while higher process yields are obtained compared to other approaches followed in literature. Then, quality of CNC-NP is improved compared to CNC-ONP.

Finally, in the case of CNC-NP-B, cost increases not only by the use of NP but also due to the high chemical and energy consume during pretreatments. In addition, there is a significantly lower process yield compared to the other two previous approaches (35% vs. around 60%) due to the extensive removal of impurities before acid hydrolysis. The quality of CNC-NP-B is of course greater, however, the associated costs for its production are much higher than any of the other two direct approaches for obtaining CNC. Furthermore, it is questionable the sustainability of these production processes in which pretreatment losses are so high. It is probably a better option to use high quality raw materials such as virgin fibers to avoid all these losses and use recycled fibers to other less demanding uses such as newsprint production in which the yields are significantly higher.

4. CONCLUSIONS

To the best knowledge of the authors, CNC have been only produced with a previous isolation of cellulose particles. This purification treatments suppose an increment in costs due to chemical and energy consumption and the low process yield because of the high pretreatment losses. However, this study proves the viability of a direct production of CNC from recycled papers.

CNC produced from ONP and NP present similar properties. However, the cost of ONP is around five times lower than that of NP. Therefore, in applications where presence of inks is not a problem, i.e. for example high-strength papers, CNC produced from ONP would be an interesting option to improve their properties at low cost.

On the other side, CNC-NP-B present a higher purity and quality compared to CNC-ONP and CNC-NP. Despite the increment in costs because of the low process yield, CNC-NP-B are still a more sustainable and economic option than CNC-MCC, where the cost of raw material is strongly higher. In addition, their properties are quite similar, opening their range of applications.

Therefore, each produced CNC can be applied in different applications, depending on quality requirements. When high quality CNC are needed, CNC-NP-B will be the best candidate. However, applications where presence of impurities is not an inconvenience, like cement or packaging paper and cardboard, CNC-ONP and CNC-NP can be used due to their lower cost, thus promoting an extended use of CNC and avoiding a large volume of ONP being used in less sustainable applications.

5. ACKNOWLEDGEMENTS

This study has been supported by the project “NANOSOLPAPELREC” (Ref. CTQ2013-48090-C2-1-R) and the grant of C. Campano (BES-2014-068177), from the Spanish Ministry of Economy and Competitiveness. Authors also wish to acknowledge Francisco Caballero and Cristina Villagrasa for their collaboration in the experimental work.

6. REFERENCES

- Biedermann, M., & Grob, K. (2010). Is recycled newspaper suitable for food contact materials? Technical grade mineral oils from printing inks. *European Food Research and Technology*, 230(5), 785-796.
- Čabalová, I., Kačík, F., Geffert, A., & Kačíková, D. (2011). The effects of paper recycling and its environmental impact. *Environmental Management in Practice*, 329-350.
- Campano, C., Balea, A., Blanco, A., & Negro, C. (2016). Enhancement of the fermentation process and properties of bacterial cellulose: a review. *Cellulose*, 23(1), 57-91.
- Canetti, M., Bertini, F., De Chirico, A., & Audisio, G. (2006). Thermal degradation behaviour of isotactic polypropylene blended with lignin. *Polymer Degradation and Stability*, 91(3), 494-498.
- Csiszar, E., Kalic, P., Kobol, A., & Ferreira, E. D. (2016). The effect of low frequency ultrasound on the production and properties of nanocrystalline cellulose suspensions and films. *Ultrasonics Sonochemistry*, 31, 473-480.
- Chen, L. H., Wang, Q. Q., Hirth, K., Baez, C., Agarwal, U. P., & Zhu, J. Y. (2015). Tailoring the yield and characteristics of wood cellulose nanocrystals (CNC) using concentrated acid hydrolysis. *Cellulose*, 22(3), 1753-1762.
- Danial, W. H., Majid, Z. A., Muhid, M. N. M., Triwahyono, S., Bakar, M. B., & Ramli, Z. (2015). The reuse of wastepaper for the extraction of cellulose nanocrystals. *Carbohydrate Polymers*, 118, 165-169.

- Delgado-Aguilar, M., Tarres, Q., Pelach, M. A., Mutje, P., & Fullana-i-Palmer, P. (2015). Are Cellulose Nanofibers a Solution for a More Circular Economy of Paper Products? *Environmental Science & Technology*, 49(20), 12206-12213.
- Donnet, J.-B. (1993). *Carbon black: science and technology*: CRC Press.
- Du, H. S., Liu, C., Mu, X. D., Gong, W. B., Lv, D., Hong, Y. M., Si, C. L., & Li, B. (2016). Preparation and characterization of thermally stable cellulose nanocrystals via a sustainable approach of FeCl₃-catalyzed formic acid hydrolysis. *Cellulose*, 23(4), 2389-2407.
- Dufresne, A. (2012). *Nanocellulose: from nature to high performance tailored materials*: Walter de Gruyter.
- Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J.-L., Heux, L., Dubreuil, F., & Rochas, C. (2007). The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacromolecules*, 9(1), 57-65.
- French, A. D., & Cintron, M. S. (2013). Cellulose polymorphy, crystallite size, and the Segal Crystallinity Index. *Cellulose*, 20(1), 583-588.
- Habibi, Y. (2014). Key advances in the chemical modification of nanocelluloses. *Chemical Society Reviews*, 43(5), 1519-1542.
- Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chemical reviews*, 110(6), 3479-3500.
- Hamad, W. Y., & Hu, T. Q. (2010). Structure-process-yield interrelations in nanocrystalline cellulose extraction. *Canadian Journal of Chemical Engineering*, 88(3), 392-402.
- Henriksson, M., Berglund, L. A., Isaksson, P., Lindstrom, T., & Nishino, T. (2008). Cellulose nanopaper structures of high toughness. *Biomacromolecules*, 9(6), 1579-1585.
- Hu, Y., Tang, L., Lu, Q., Wang, S., Chen, X., & Huang, B. (2014). Preparation of cellulose nanocrystals and carboxylated cellulose nanocrystals from borer powder of bamboo. *Cellulose*, 21(3), 1611-1618.
- Lourenco, A. F., Gamelas, J. A. F., & Ferreira, P. J. (2014). Increase of the filler content in papermaking by using a silica-coated PCC filler. *Nordic Pulp & Paper Research Journal*, 29(2), 240-245.
- Lu, P., & Hsieh, Y.-L. (2012). Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohydrate Polymers*, 87(1), 564-573.
- Martínez-Sanz, M., Vicente, A., Gontard, N., Lopez-Rubio, A., & Lagaron, J. (2015). On the extraction of cellulose nanowhiskers from food by-products and their comparative reinforcing effect on a polyhydroxybutyrate-co-valerate polymer. *Cellulose*, 22(1), 535-551.
- Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Asri, S., & Ismail, A. F. (2015). Physicochemical properties of "green" nanocrystalline cellulose isolated from recycled newspaper. *Rsc Advances*, 5(38), 29842-29849.
- Peresin, M. S., Habibi, Y., Zoppe, J. O., Pawlak, J. J., & Rojas, O. J. (2010). Nanofiber Composites of Polyvinyl Alcohol and Cellulose Nanocrystals: Manufacture and Characterization. *Biomacromolecules*, 11(3), 674-681.
- Ranby, B. G. (1951). Cellulose and muscle- The colloidal properties of cellulose micelles. *Discussions of the Faraday Society*(11), 158-&.
- Roman, M., & Winter, W. T. (2004). Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules*, 5(5), 1671-1677.

- Sanders, J. P., & Gallagher, P. K. (2002). Kinetic analyses using simultaneous TG/DSC measurements: Part I: decomposition of calcium carbonate in argon. *Thermochimica Acta*, 388(1-2), 115-128.
- Segal, L., Creely, J. J., Martin, A. E., & Conrad, C. M. (1959). An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Textile Research Journal*, 29(10), 786-794.
- Sheltami, R. M., Abdullah, I., Ahmad, I., Dufresne, A., & Kargarzadeh, H. (2012). Extraction of cellulose nanocrystals from mengkuang leaves (*Pandanus tectorius*). *Carbohydrate Polymers*, 88(2), 772-779.
- Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83(1), 1-11.
- Tasman, J. E., & Berzins, V. (1957). The Permanganate Consumption of Pulp Materials. *Tappi*, 40(9), 691-704.
- Wang, N., Ding, E., & Cheng, R. (2007). Thermal degradation behaviors of spherical cellulose nanocrystals with sulfate groups. *Polymer*, 48(12), 3486-3493.
- Wang, Q. Q., Zhu, J. Y., Reiner, R. S., Verrill, S. P., Baxa, U., & McNeil, S. E. (2012). Approaching zero cellulose loss in cellulose nanocrystal (CNC) production: recovery and characterization of cellulosic solid residues (CSR) and CNC. *Cellulose*, 19(6), 2033-2047.
- Xu, Q. H., Gao, Y., Qin, M. H., Wu, K. L., Fu, Y. J., & Zhao, J. (2013). Nanocrystalline cellulose from aspen kraft pulp and its application in deinked pulp. *International Journal of Biological Macromolecules*, 60, 241-247.
- Zhang, Y., Lu, X. B., Chen, W., & Lv, W. J. (2012). *Preparation and characterization of nanocrystalline cellulose from bamboo fibers by controlled cellulase hydrolysis*. Nanjing: Nanjing Forestry Univ.

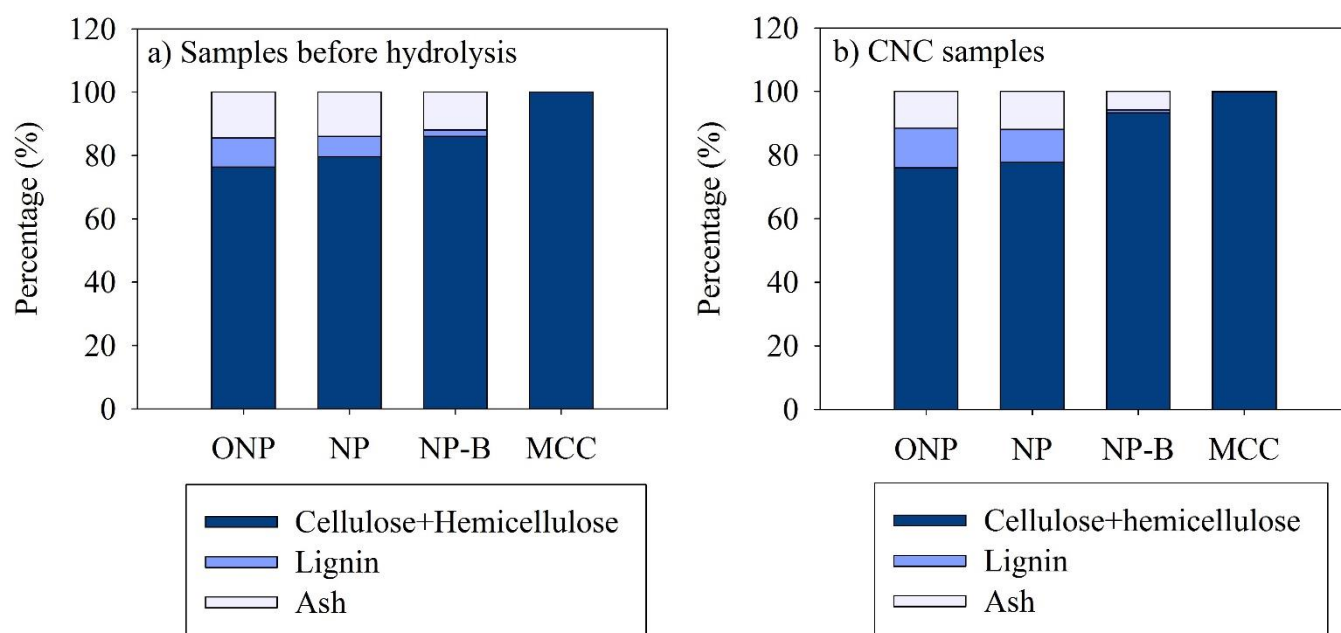


Figure 1. Proportion of cellulose+hemicellulose, lignin and ash in a) samples before hydrolysis and b) obtained CNC.

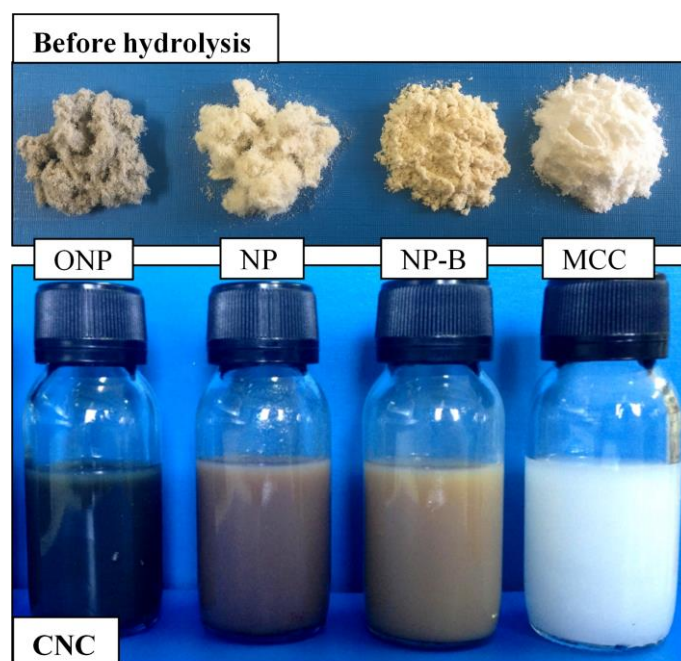


Figure 2. Macroscopic images of sample before hydrolysis at the top and obtained CNC at the bottom for ONP, NP, NP-B and MCC.

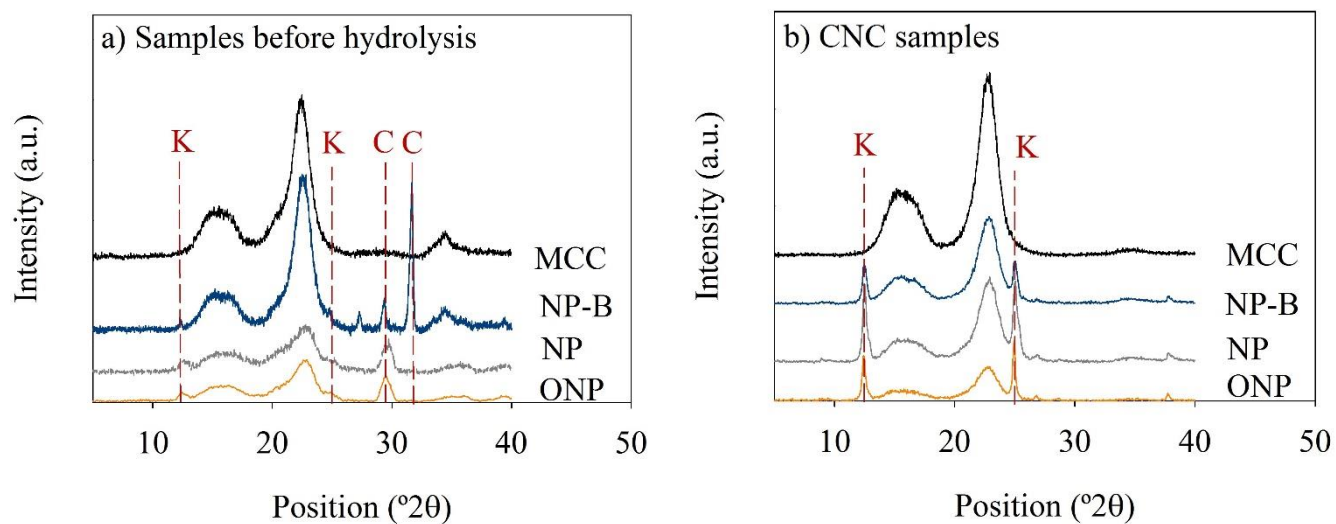


Figure 3. XRD patterns of a) MCC, NP-B, NP and ONP and b) CNC-MCC, CNC-NP-B, CNC-NP and CNC-ONP. *K is representing kaolinite and C means CaCO_3 .

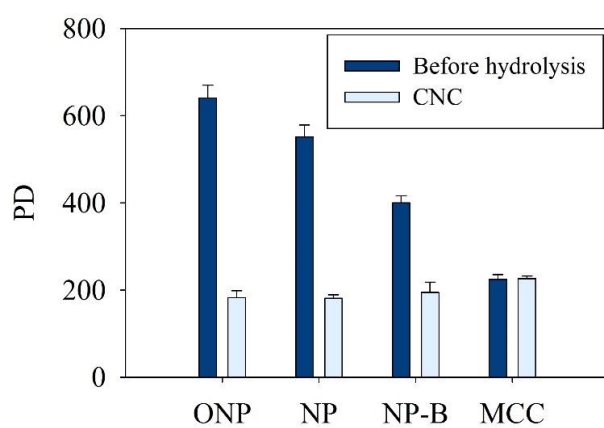


Figure 4. PD of samples before hydrolysis and obtained CNC.

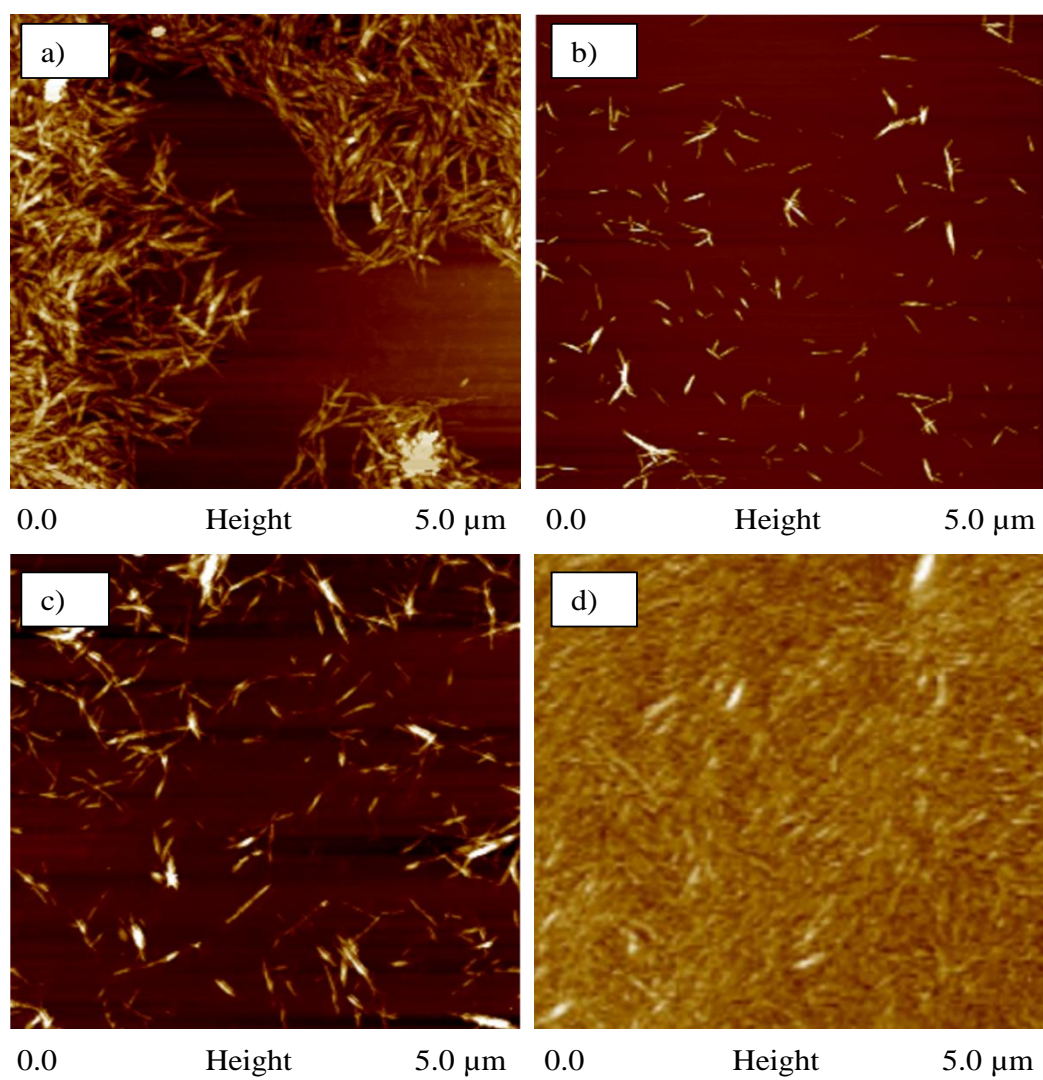


Figure 5. AFM images of a) CNC-ONP, b) CNC-NP, c) CNC-NP-B and d) CNC-MCC.

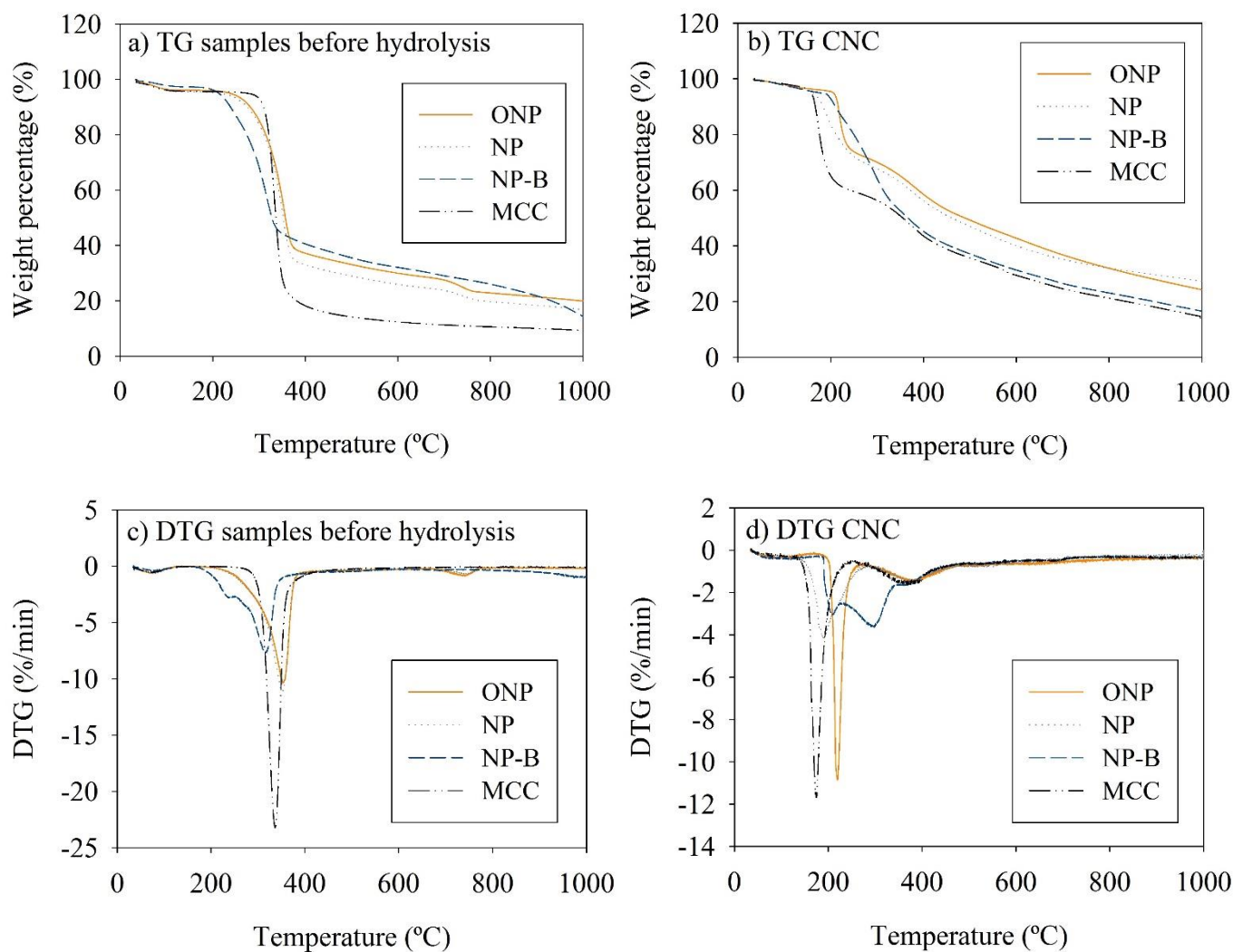
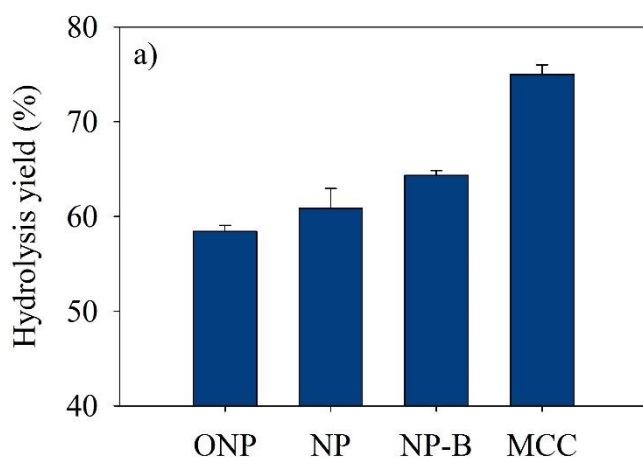


Figure 6. TG curves of a) samples before hydrolysis and b) produced CNC and DTG curves of c) samples before hydrolysis and d) CNC.



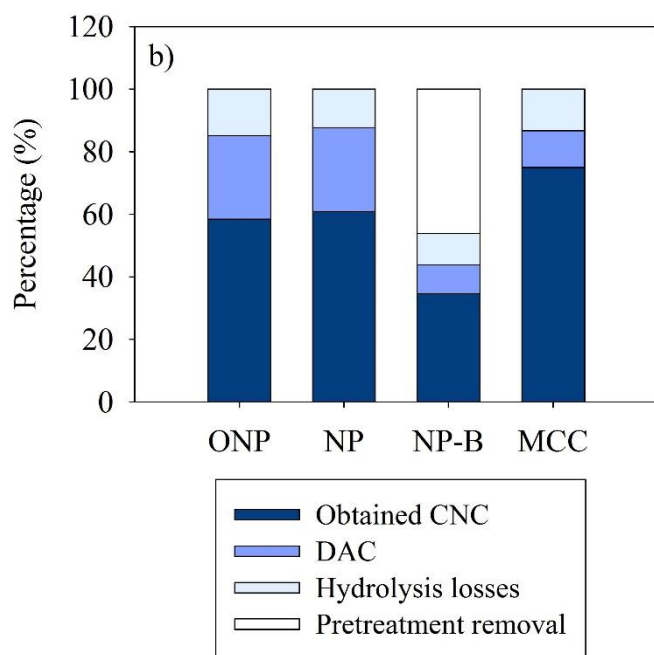


Figure 7. a) Hydrolysis yield and b) Process yield, DAC, hydrolysis losses and pretreatment removal percentages referred to initial dry mass of papers of all obtained CNC.

Table 1. Comparison of CNC properties produced from ONP, NP, NP-B and MCC.

	CNC-ONP	CNC-NP	CNC-NP-B	CNC-MCC
CNC purity (%)	76.0	77.8	93.3	99.9
Ash 525°C (%)	11.5	11.9	5.7	0.1
Lignin (%)	12.5	10.2	0.9	0.0
Color	Black	Brown	Beige	White
Cr.I (%)	92.6	93.4	94.8	95.5
ACD (nm)	32.5	41.2	45	54.9
PD	182	181	194	226
Aspect ratio	50-200	50-90	50-120	2-70*
Hydrolysis yield (%)	58.4	60.8	64.3	75.0

*Bibliographic data (Elazzouzi-Hafraoui et al., 2007)