Science of the Total Environment 874 (2023) 162482

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sustainability of cellulose micro-/nanofibers: A comparative life cycle assessment of pathway technologies

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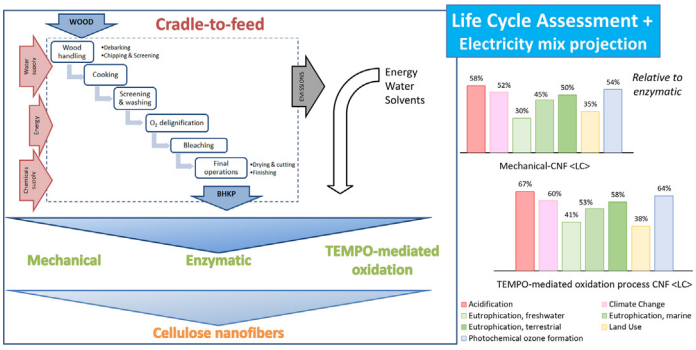
HIGHLIGHTS

- Following three different pre-treatments defines environmental priorities.
- It is proposed that functional unit should be normalized for each process.
- TEMPO-mediated oxidation is greener than the enzymatic process for CNF production.
- A fully mechanical process showed the least environmental impact for CNF production.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jacopo Bacenetti

Keywords:
Enzymatic hydrolysis
Life cycle assessment
Mechanical treatment
Nanocellulose
Pulp and paper
TEMPO-oxidized cellulose nanofibrils

ABSTRACT

Cellulose micro- and nanofibers (CNFs) are commonly regarded as "greener" than petro-based materials. The high energy input that their production still demands, along with the use of chemicals or heat in some pretreatments, asks for a critical view. This paper attempts a life cycle assessment of CNFs produced from bleached hardwood kraft pulp via three different pre-treatments before mechanical homogenization. First, a fully mechanical route, based on a Valley beating pre-treatment. Second, an enzymatic route, based on endoglucanases and requiring certain temperature (~50 °C). Third, a TEMPO-mediated oxidation route, considering not only the impact of the chemical treatment itself but also the production of TEMPO from ammonia and acetone. The main output of the study is that both, mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. Although the mechanical route presents slightly milder contributions to climate change, acidification, eutrophication, and other indicators, saying that TEMPO-mediated oxidation is environmentally unfeasible should be put under question. After all, and despite being disregarded in most assessment publications up to date, it is the only well-known way to selectively oxidize primary hydroxyl groups and thus producing kinds of CNFs that are unthinkable by other ways.

Abbreviations: BHKP, bleached hardwood kraft pulp; CMNF, cellulos micro- nano- fiber; CNF, cellulose nanofiber; FW, freshwater; ILCD, International Life Cycle Data system; LCA, life cycle assessment; LCI, life cycle inventory; LCIA, life cycle impact assessment; M, marine; PEF, product environmental footprint; POF, photochemical ozone formation; T, terrestrial; TAA, triacetonamine; TEMP, 2,2,6,6-tetramethylpiperidine; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxy.

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http://dx.doi.org/10.1016/j.scitotenv.2023.162482
Received 23 January 2023; Received in revised form 21 February 2023; Accepted 22 February 2023
Available online 27 February 2023

1. Introduction

The concept *nanocellulose* is generally found as an umbrella term encompassing, besides cellulose nanocrystals and bacterial cellulose, both micro- and nanofibrillated cellulose. These cellulose micro- and nanofibers (CMNFs) are increasing their presence in different application fields: i) paper and packaging products, where nanocellulose is used as filler, coating component, barrier properties enhancer or plastic films replacement (Lavoine et al., 2012; Paunonen, 2013; Hubbe, 2014; Kim et al., 2015; Kisonen et al., 2015); ii) high-end technological applications, such as adhesives, hierarchical materials, electroacoustic devices, sensors and electronics (Eichhorn et al., 2010; Kawahara et al., 2013; Timofeev et al., 2014; Kim et al., 2015); iii) low-weight engineering applications, such as green composites, interior automotive applications, foams, ultra-filtrating membranes, and insulation materials (Eichhorn et al., 2010; Siró and Plackett, 2010); or iv) biomedical applications, as a carrier for drug delivery or as a scaffold for tissue engineering (Eichhorn et al., 2010; Siró and Plackett, 2010; Plackett et al., 2014; Jorfi and Foster, 2015). It is worth to mention that mineral fillers, in addition to organic ones, are also used to improve properties of materials in different applications (Civancik-Uslu et al., 2018).

The nanocellulose market value worldwide in 2020 was estimated in 297 million US dollars and it is forecasted to grow up to 783 million US dollars by 2025 (Statista, 2020). CMNFs will compete in the future with cement as reinforcement material, with plastic in packaging markets, with synthetic binders in coating processes, with cotton in hygiene and absorbent products, with carbon fiber in reinforced composites used in automotive and aerospace components, with fiberglass in insulation applications, with silica aerogels in the oil and gas industry, and with other future novel applications (Cowie et al., 2014). The environmental performance of CMNFs may be an issue when deciding to use them in all these possible markets and with massive productions.

Several production methods to transform the individual cellulosic fibers into microfibrils or nanofibrils have been introduced, although they are mainly optimized at the laboratory level (Rebouillat and Pla, 2013). Generally speaking, a nanofibrillation stage, often by means of a high-pressure homogenizer (HPH), follows a certain pre-treatment, which is key to avoid clogging and excessive energy consumption. The most popular pre-treatments are mechanical beating (Hubbe et al., 2008; Stelte and Sanadi, 2009; Siró and Plackett, 2010), acid hydrolysis (Marchessault et al., 1959; Stelte and Sanadi, 2009; Siró and Plackett, 2010), enzymatic hydrolysis (Marchessault et al., 1959; Siró and Plackett, 2010), carboxymethylation (Arvidsson et al., 2015; Si et al., 2022), and oxidation of hydroxyl groups. The latter is usually mediated by sodium periodate or by 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) (Liimatainen et al., 2012; Patiño-Masó et al., 2019; Filipova et al., 2020; Serra-Parareda et al., 2021b).

However, there are few publications on the environmental assessment of these production processes. Previous life cycle assessment (LCA) studies on CMNFs comprise: i) comparison of carboxymethylation and enzymatic hydrolysiss before nanofibrillation (Nguyen, 2014; Arvidsson et al., 2015), ii) comparison of carboxymethylation and TEMPO-mediated oxidation (Li et al., 2013), iii) energy consumption assessment of a nanocellulose production method that combined mechanical shear stress with hot-compressed water treatment (Sun et al., 2013), iv) cellulose nanowhiskers based on mechanical and chemical acid treatments (De Figueirêdo et al., 2012), and v) lignocellulosic nanofibers to increase the number of times that paper can be recycled in a circular economy (Delgado-Aguilar et al., 2015). Tangentially to the topic, an attributional LCA of woodchip production (Neupane et al., 2011), the influence of time in life cycle assessments (Sazdovski et al., 2022), a sustainability study (techno-economic and environmental analysis) of paper pulp reinforced with CMNF (Serra-Parareda et al., 2022), a cradle-to-gate LCA of the *Eucalyptus globulus* short-rotation plantations and chips extraction in Chile (Morales et al., 2015), the assessment of delignification as a pre-treatment for a nanolignin synthesis process (Teh et al., 2021), and a case study of peracetic acid bleaching of wood pulp (Echeverria et al., 2021) are worthy of mention.

In most of these publications, chemical pre-treatment routes presented higher environmental impacts. Nonetheless, due to lack of data, numerous assumptions were considered. Comparing chemical modifications (substitution, oxidation) to mechanical treatments or depolymerizations is not a straightforward task, as the very nature of the material produced is different. Furthermore, TEMPO-mediated oxidation is often disregarded for its unfeasibility, despite being actually carried out by major companies like Nippon Paper, at least for high value-added products (Nippon Paper Group, 2019). By generating carboxylate groups, which are easily hydrated and carry negatively charge, chemical pre-treatments promote steric and electrostatic repulsion between like-charged cellulose chains. This allows for higher yields during the second stage of the process (nanofibrillation), being able to attain samples consisting entirely of cellulose nanofibers (CNFs). For the sake of simplicity and comparison, and in a possible inaccurate but common decision, we will henceforth refer to all fibrillated products in this work as “CNFs”, even if they contain microfibers.

This paper deals with an LCA of CNFs produced via three different pre-treatments before the nanofibrils are separated by mechanical homogenization: 1) a fully mechanical route based on a refining pre-treatment; 2) an enzymatic route, and 3) a TEMPO-mediated oxidation route.

The functional unit (FU) serves as the reference basis of the calculation related with the environmental impacts of the system under study. However, when a cradle to gate LCA is being performed for chemical processes, there might be variables which affect to the function of the final product. Although this takes place outside of the cradle to gate boundaries, these issues should be accounted as valuable additional information. Specially when we are comparing among different alternatives.

The preliminary functional unit was 1 kg of nanocellulose on dry basis. Nonetheless, since the different pre-treatments end up resulting in products of different properties, the functional unit is then corrected (normalized) on basis of the final properties promoted by these nanofibrillated cellulose products. In the case of this work, it is assumed that the intended use is the reinforcement of paper. For instance, similar methodology is applied in module D within the EN 15804:2012 + A2:2019 for construction products LCA (Albertí et al., 2019; European Standards, 2019).

2. Methodology and materials

2.1. Primary and secondary data

Primary data consist of the independent variables chosen along the experimentation, plus measurements of certain dependent variables. The former include the amounts of reagents and water spent in each case, the temperature, the extent of mechanical refining, the stirrers' settings, and the pressure and number of cycles. Their values chosen for modelling are not arbitrary, but resulting from the experience of the group and optimization studies (Tarrés et al., 2017; Serra et al., 2017; Serra-Parareda et al., 2021a; Aguado et al., 2022).

The source of cellulose was a bleached hardwood kraft pulp (BHKP), taken as a commercial product from a pulp mill. The materials and procedures to treat this cellulosic pulp by mechanical beating, enzymatic hydrolysis and TEMPO-mediated oxidation can be found in detail in the above-cited works. Briefly, reagents for the enzymatic process included Novozym 476 from Novozymes A/S (Denmark) and a buffer consisting of acetic acid and sodium acetate, both from Sigma-Aldrich (Barcelona, Spain). The oxidation, on the other hand, required TEMPO, NaBr, NaClO, and NaOH, which were likewise obtained from Sigma-Aldrich. Needless to say, the fully mechanical process is chemical-free. Distilled water was consistently used in all cases. The fibrillation process was carried out in a HPH, NS1001L PANDA 2 K-GEA, following all the pre-treatments. It run at 2 % consistency, 3 times at 300 bar and 7 times at 600 bar.

The main dependent variable to be measured was energy consumption. It was determined using a device from Circutor (Barcelona, Spain), CVM-C10, which gives values of the power and current intensity required from the electrical grid. Considering previous works performed within the

research group (González et al., 2012; Delgado-Aguilar et al., 2015; Tarrés et al., 2016), CNFs from BHKP were used for paper reinforcement. Handsheets obtained with a dosage of 3 wt% of CNFs in bulk and 97 wt% BHKP were mechanically characterized for tensile strength, as ISO 1924-2 describes (ISO, 2008).

Scanning Electron Microscopy (SEM) was conducted to qualitatively assess the morphology of the obtained CNFs. The sample preparation consisted on the formation of a nanopaper by means of solvent casting, pouring a suspension of CNFs at 0.2 wt% consistency in a petri dish and drying it at low temperature. The resulting nanopapers were released from the petri dish and observed in a Hitachi S-3000 microscope, working at 7 kV; samples were previously covered with carbon via sputtering.

All the secondary data consulted has been checked under the criteria defined in the pedigree matrix (reliability, completeness, temporal correlation, geographical correlation and technological correlation) (Weidema and Wesnæs, 1996; Ciroth, 2009). Further references can be found below, depending on the specific process to be modelled.

2.2. Life cycle assessment

LCA is a holistic and comprehensive methodology for assessing the environmental loads and potential impacts of a product, process, or service in each stage of its life cycle, from the extraction of the materials to the management of the disposed product after its use (cradle-to-grave). Following the ISO standards 14040:2006 (ISO, 2020) and 14044:2006 (ISO, 2007), its results were structured within the following stepwise procedure: goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA), and interpretation of results. Out of the possible environmental performance indicators (Baumann and Tillman, 2004; Molander et al., 2004; Puig et al., 2013), we decided to evaluate Global Warming Potential, Acidification Potential, Nutrient Enrichment, Photochemical Ozone Formation, Primary Energy Consumption and Use of Agricultural Land.

The LCA was developed also following the product environmental footprint (PEF) methodology, which has been fostered by the European Commission (Manfredi et al., 2012; European Commission, 2013). Environmental impacts were calculated using the GaBi Professional Software (version 10.6.1.35) for LCA. This was performed by 1) considering the impacts of the input material flows, 2) adding the impacts of the output material flows post-treatments, 3) adding the thermal energy demand and 4) adding the mechanical energy demand.

3. Modelling

3.1. Generalities

Each of the pre-treatments considered (mechanical, enzymatic, and oxidative) may include more than one unit operation. Unit operations may be inexcusable, as in the case of washing to remove the excessive amounts of salts generated along TEMPO-mediated oxidation, or seemingly optional but experimentally proven necessary to reach the desired outcome, as in the refining step to ease enzymatic hydrolysis.

In all these possible routes, the pulp and the micro- and nanofibers from it are computed on a dry basis, even though they are moist at all times. The impact of electricity consumption corresponds to the European average electricity mix from the year 2018 according to GaBi databases (Sphera, 2021). Energy balances considered these electricity inputs. Mass balances were performed choosing 1 kg BHKP as the calculation basis and neglecting the loss of cellulosic materials by filtration.

3.2. Pulp production

The overall impact of the CNF production depends both on the feedstock (cellulose fiber) and on what technology we apply to this feedstock. Various publications deal with CNFs produced from different feedstocks, including in the spectrum of wood, cane, straw, leaf, bast, fruit and seed (Jonoobi et al., 2015). Because of this wide range of raw materials and previous experience by the authors, we have decided to use one specific stock: eucalyptus wood treated using kraft pulping and bleaching. Kraft pulp production is the dominant pulp-making process due to the high quality of the resulting printing paper, liner, fluting, and other products whose strength is of utmost importance. A pulp mill comprises highly energy-intensive procedures such as debarking, chip refining, cooking, washing, screening, bleaching, further washing, and drying. A simplified diagram of the production process of BHKP is shown in Fig. 1.

The best available techniques to produce pulp, paper and board were established under the EU Commission Implementing Decision of 26 September 2014. The first paper analyzing the environmental life cycle effects of the European pulp and paper industry was published in 1996 (Bloemhof-Ruwaard et al., 1996). Probably, the most relevant reference using the feedstock selected in this study is the one on environmental impact assessment of total chlorine-free pulp from *Eucalyptus globulus* in Spain (González-García et al., 2009). It concludes that inherent activities related to BHKP such as cooking, bleaching and wastewater treatment are not always the main contributors to the environmental impact of the process. Upstream chemical and fuel productions, besides on-site energy production systems, seem to be important contributors to different impact categories (Lopes et al., 2003; Das and Houtman, 2004; Gemechu et al., 2013).

The LCA for the BHKP production feedstock has been calculated with the available GaBi databases (Sphera, 2021). It includes activities such as forest management, sawmilling, logs storing, debarking, and milling. Given that this pulping process is common to all CNFs considered, the uncertainty associated to this process affects the three pre-treatments.

3.2.1. Mechanical pre-treatment

The mechanical production process of cellulose nanofibers involved a refining process in a Valley pile as the main step. 1 kg dry BHKP was diluted to 1.57 % consistency, following TAPPI standard T200 (TAPPI, 2020), to proceed with refining for 3 h. When the refining process stopped, the sample was filtrated to a consistency of 20 %, not requiring washing. An amount of this sample was taken, diluted with tap water at 2 % consistency, and homogenized to obtain a dilute suspension of micro- and nanofibers. Fig. 2 shows the different steps followed in the mechanical production process of CNFs. In the absence of chemicals, the most relevant environmental impacts lie in water consumption, although much of it is recycled, and electricity inputs.

3.2.2. Enzymatic hydrolysis

Owing to the high specificity of enzymes, generally speaking, their main objectives are to increase the quality of product, yield, while reducing energy and chemicals consumption, hopefully converting traditional processes into “green” ones (Nielsen et al., 2007). Nonetheless, the extent to which the crystallinity of cellulose prevents the access of glucanases to the acetal bonds, the failure to hydrolyze them at room temperature, the need for pH control, and the slow rate of reaction compel us to adopt a critical attitude in this case. Moreover, the enzymatic process to obtain CNFs involves some additional steps in comparison with the mechanical one. The schematic process of the enzymatic experiments is presented in Fig. 3.

1 kg dry BHKP was diluted to 1.5 % consistency and disintegrated for 20 min at 3000 rpm (60,000 revs.), following the ISO 5263-1 standard (ISO, 2004). When the disintegration process stopped, the sample was filtrated to 20 % consistency and, after that, an additional dilution at 10 % consistency was done on the pulp sample, which was next refined in a PFI mill to 4000 revs. The enzymatic hydrolysis needs to maintain a pH of around 5. To comply with this, the next dilution step to 5 % consistency was done with a buffer solution, where 95.8 g of sodium acetate and 16.92 mL of acetic acid per liter of solution were added. After the buffer dilution, the enzymatic hydrolysis was performed by supplying Novozym at a concentration of 0.83 %. During the enzymatic treatment, the temperature was maintained at 50 °C, and the contact time was 180 min.

Novozym 476 is a mono-component endoglucanase with a cellulose-binding domain which preferably degrades cellulose in the unordered

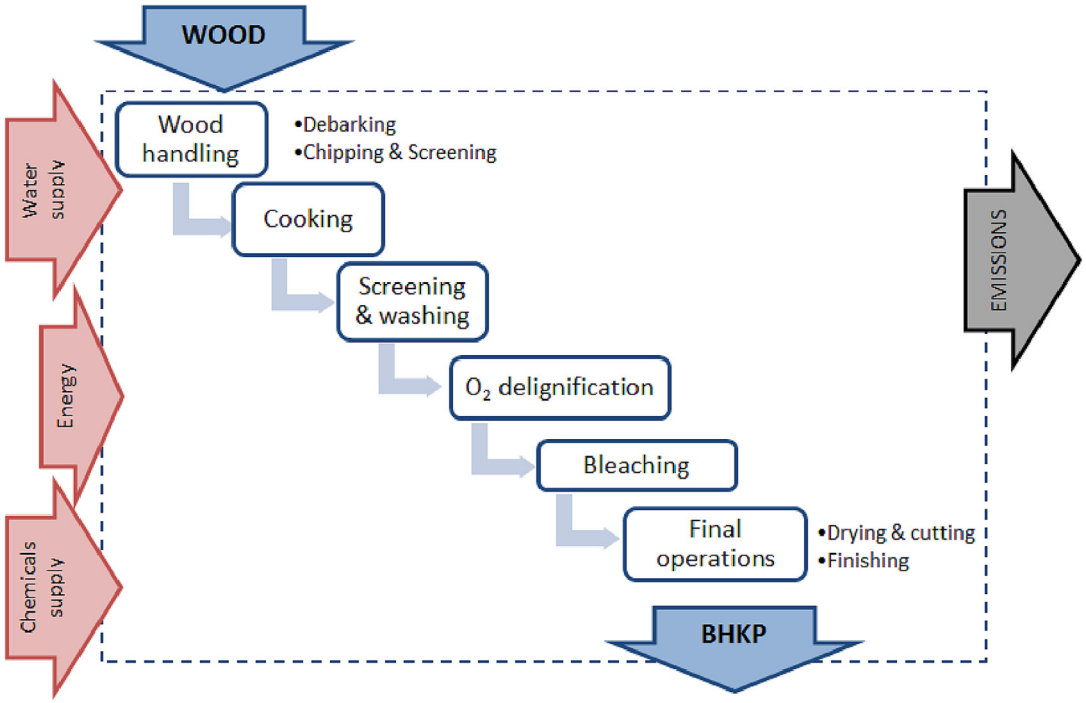
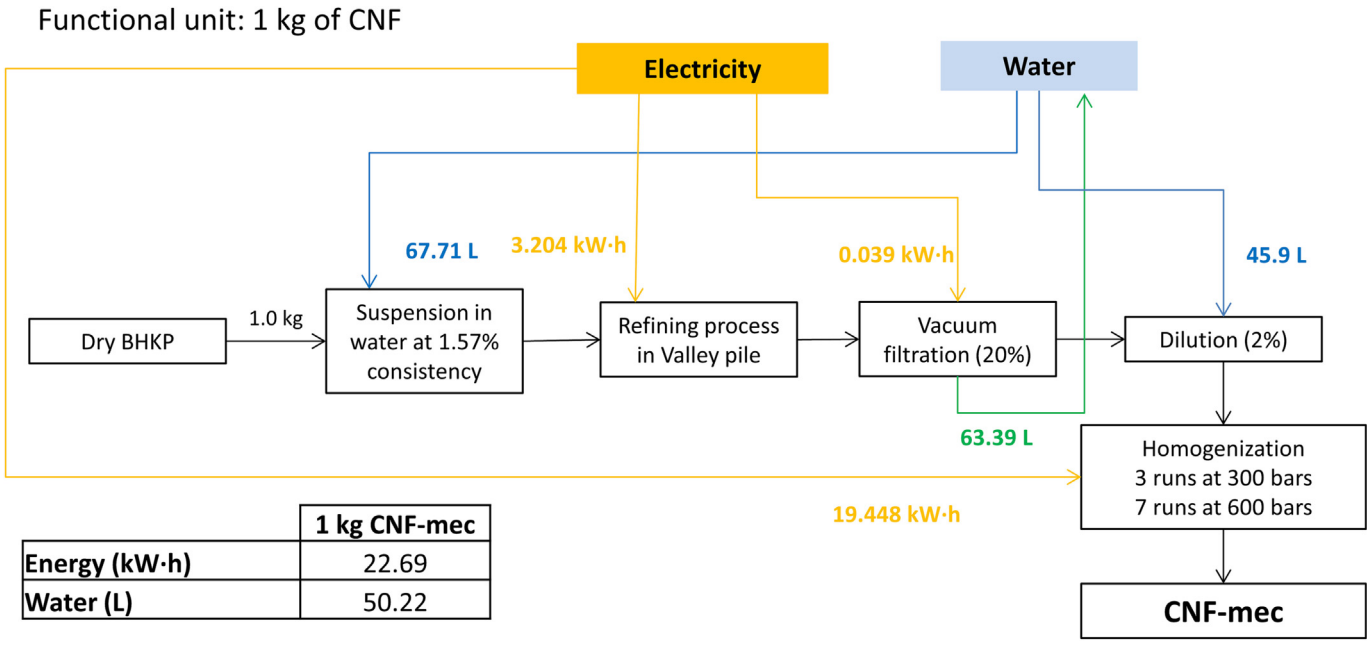


Fig. 1. Flowchart of an industrial process to obtain bleached hardwood kraft pulp (BHKP).

regions. This glucanase is produced from a genetically modified strain of *Aspergillus fungus*. The cellulolytic activity is 5000 endocellulose units per gram of material, i.e., 5000 ECU/g (Köpeke et al., 2008). The product was delivered in aqueous suspension. After the reaction, an increase in bath temperature to 80 °C deactivated the enzyme. The product was diluted to 2 % consistency and homogenized to obtain micro- and nanofibers.

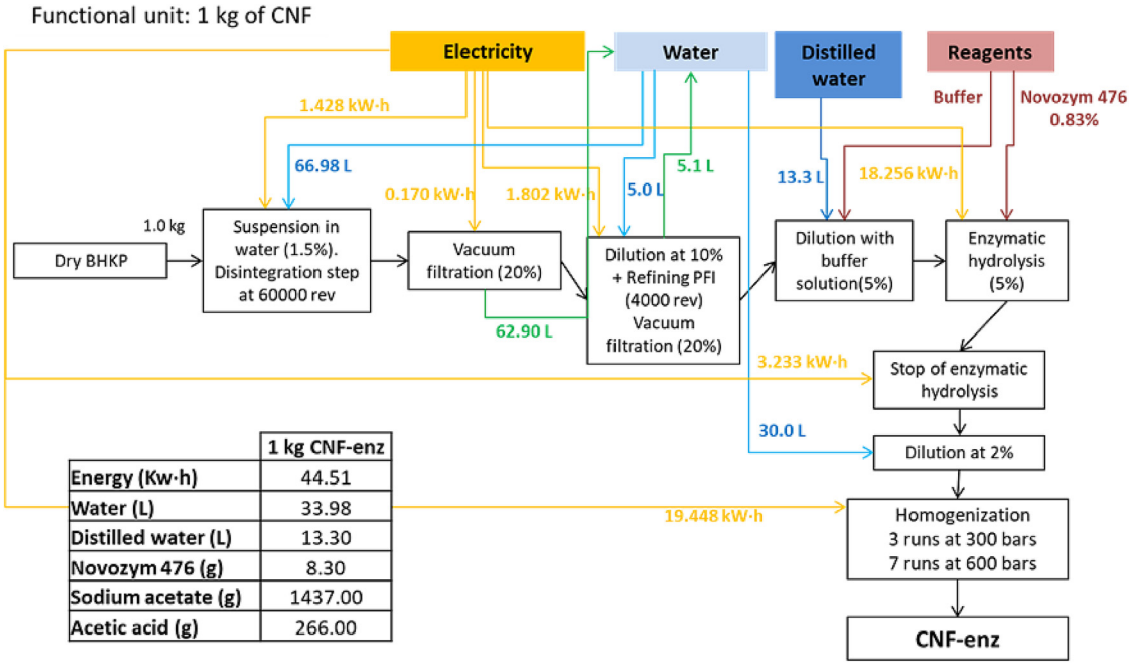
From the literature (Nielsen et al., 2007; Skals et al., 2008; Jegannathan and Nielsen, 2013; Liptow et al., 2013), we extracted valuable information about environmental impacts of Novozym 476. An exhaustive study used five types of enzymes in a cradle-to-gate impact assessment (Nielsen et al., 2007), covering primary energy consumption (88 MJ/kg of the final product), global warming (7.53 kg CO_2 eq/kg of the final product), acidification (23.77 g SO_2 eq/kg of the final product), nutrient enrichment (21.6 g PO_4 eq/kg of the final product), photochemical ozone formation (2.71 g ethylene eq/kg of the final product) and use of agricultural land (3.46 m^2·year/kg of the final product).

The acetic acid is assumed to be produced from methanol by low-pressure carbonylation. This is the most commonly used process in the industry (Cheung et al., 2012). In turn, sodium acetate is a sodium salt produced by the neutralization of acetic acid with sodium hydroxide. The environmental factors of such neutralization were obtained with a proxy from GaBi Professional databases (Sphera, 2021), assumed to be like the neutralization of citric acid with sodium hydroxide to produce trisodium citrate (similar pK_a, similar enthalpy of neutralization). Using proxies is a



	1 kg CNF-mec
Energy (kW·h)	22.69
Water (L)	50.22

Fig. 2. Process diagram of the production of CNFs by a mechanical pre-treatment.



	1 kg CNF-enz
Energy (Kw·h)	44.51
Water (L)	33.98
Distilled water (L)	13.30
Novozym 476 (g)	8.30
Sodium acetate (g)	1437.00
Acetic acid (g)	266.00

Fig. 3. Process diagram of the production of CNFs by enzymatic pre-treatment.

common way of LCA simplification, whenever actual data is not found (Baitz et al., 2013).

3.2.3. TEMPO-mediated oxidation

This chemical process to obtain CNF is based on the use of the stable radical TEMPO, as a catalytic reagent in combination with other oxidative reagents such as sodium hypochlorite, as Fig. 4 shows. The oxidizing agent directly (and selectively) acting on primary hydroxyl groups is TEMPO itself, but it is regenerated in the process thanks to the parallel oxidation of Br^- (co-catalyst), together with the reduction of ClO^- (spent oxidizer). The process diagram is presented in Fig. 5.

The catalytic oxidation process also started with 1 kg BHKP and was suspended in tap water at a consistency of 1.5 %, before disintegrating to 15,000 revs. The subsequent reaction was performed at 1 % consistency and under alkaline conditions (Saito et al., 2007). In a typical oxidation experiment, cellulose fibers were dispersed in distilled water containing TEMPO (0.016 g per g of pulp) and NaBr (0.1 g per g of pulp). The mixture was stirred for 15 min to assure good dispersion of all the substances. After this, a 15 % NaClO solution was added dropwise to the slurry. The volume of NaClO is calculated so as to add 10 mmol per gram of cellulose. The pH was kept at 10 by the addition of 0.5 M NaOH. The increase of volume by effect of this addition was neglected. The oxidation finishes when the pH remained stable at 10. This is not included in the mass balance nor in Fig. 5 because due to its low mass fraction compared to the other reagents, it is not significant to the LCA results. The oxidized pulp was then filtered and washed with distilled water five times. Finally, the fiber suspension was cooled at room temperature before going through mechanical treatment. Fibrillation of oxidized fibers was performed by pumping the fiber suspension at 2 % consistency through the high-pressure homogenizer 3 times at 300 bars and 7 times at 600 bars of pressure.

There is only one reference in the literature that takes into account the TEMPO-mediated oxidation route in an LCA study (Li et al., 2013), but they do not include the TEMPO reagent due to the limited information in the inventory databases. In the present paper, the impact of TEMPO production is considered.

Sodium hypochlorite is produced after reacting chlorine with a sodium hydroxide solution. Those are assumed to be produced from salt (NaCl) dissolved in water, purified, and fed to an electrolysis unit. For sodium bromide, we assumed a proxy by assimilating its environmental factors to those of sodium chloride.

3.2.4. Modelling of TEMPO production

TEMPO was discovered in 1960 (Lebedev and Kazarnovskii, 1960) and is usually prepared by oxidation of 2,2,6,6-tetramethylpiperidine (TEMP) with hydrogen peroxide. The environmental data on the TEMPO production process is scarce, and the model we offer to consider its impact as part of the LCA relies on secondary data. Energy balances are estimated with an advanced calculation benchmark for industry equipment (Piccinno et al., 2016).

The modelled process starts from simple products that can be easily registered in databases (ammonia, acetone, zeolite catalysts, etc.). Direct condensation of acetone and ammonia catalyzed by zeolites produces triacetonamine (TAA) or 4-oxo-TEMP, the precursor of TEMPO (Gliozzi et al., 2014), as Fig. 6 shows. The maximum yield of this reaction is 22.6 % (Maltz et al., 2002). Better yields of TAA production (28.4 %) may be obtained from fast pyrolysis of sewage sludge using acetone as an absorption solvent but this is still not implemented at the industrial level (Cao et al., 2010).

The reaction runs as follows (see Fig. 7): mixing 34.8 g of acetone with 4 g of ammonium nitrate, adding 0.5 g of zeolite (CaY), adding 3.1 mL of 28–30 % aqueous ammonia. The mixture is stirred for 20 min. The temperature is kept between 20 and 25 °C. The best selectivity is obtained by combining a highly hydrophilic zeolite with a high acetone-ammonia feed ratio (Gliozzi et al., 2014). Reaction time is set at around 17 h to reach a yield of 22.6 % at room temperature. In the end, the relationship acetone-ammonia is 6:1. Once the reaction is finished, residual acetone is evaporated using a vacuum pump at room temperature, zeolite is filtered, and the product is washed 5 times with 60 mL of diethyl ether. The ether phase is dried with magnesium sulphate and filtered. Residual ether is evaporated, and the dry final product (TAA) is obtained.

The next step is to convert TAA using reduction with hydrazine hydrate towards an instable hydrazone, which is then cleaved in the presence of alkali into TEMPO and nitrogen (Kampmann and Stuhlmuller, 1997). For this purpose, molten TAA is mixed into a stirred vessel with hydrazine hydrate in a molar ratio of 1.5. The mixture is heated to 80–90 °C. The resulting hydrazone solution is transported to distillation bottoms at the base of a distillation column held at a temperature of 175 to 195 °C. These distillation

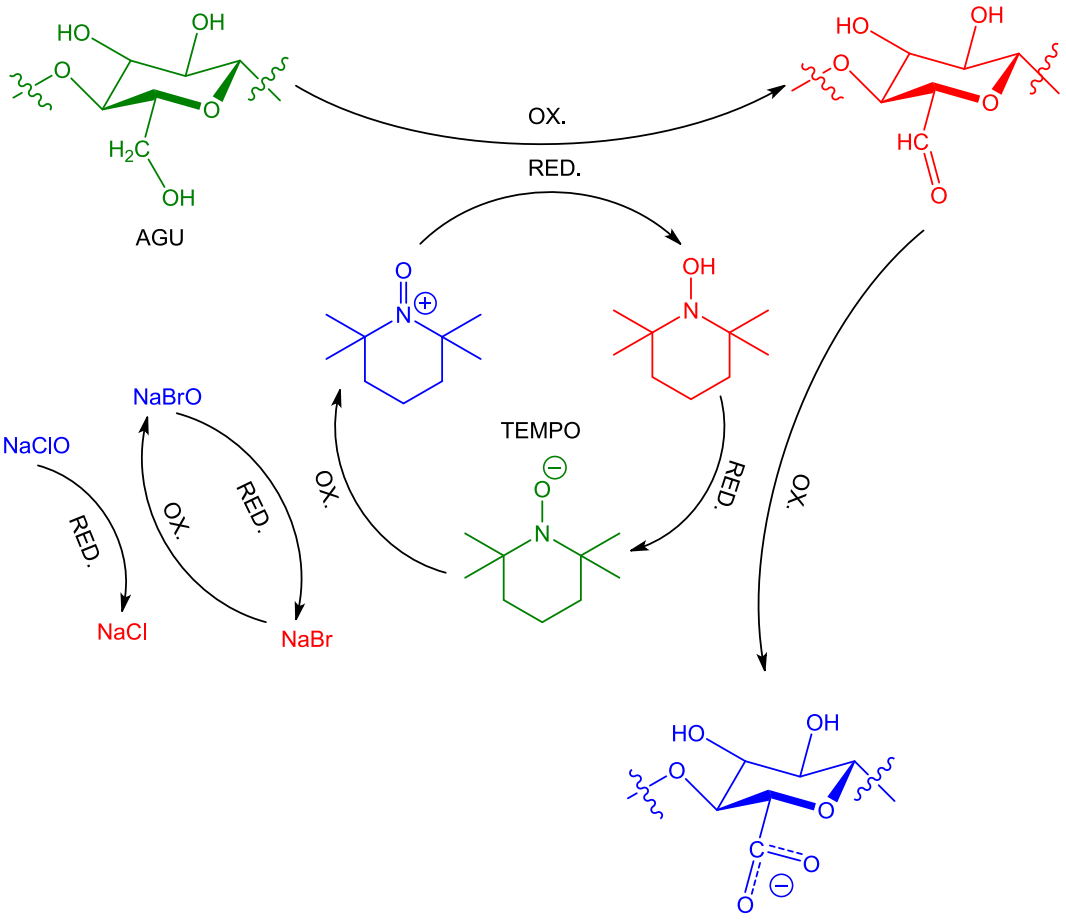
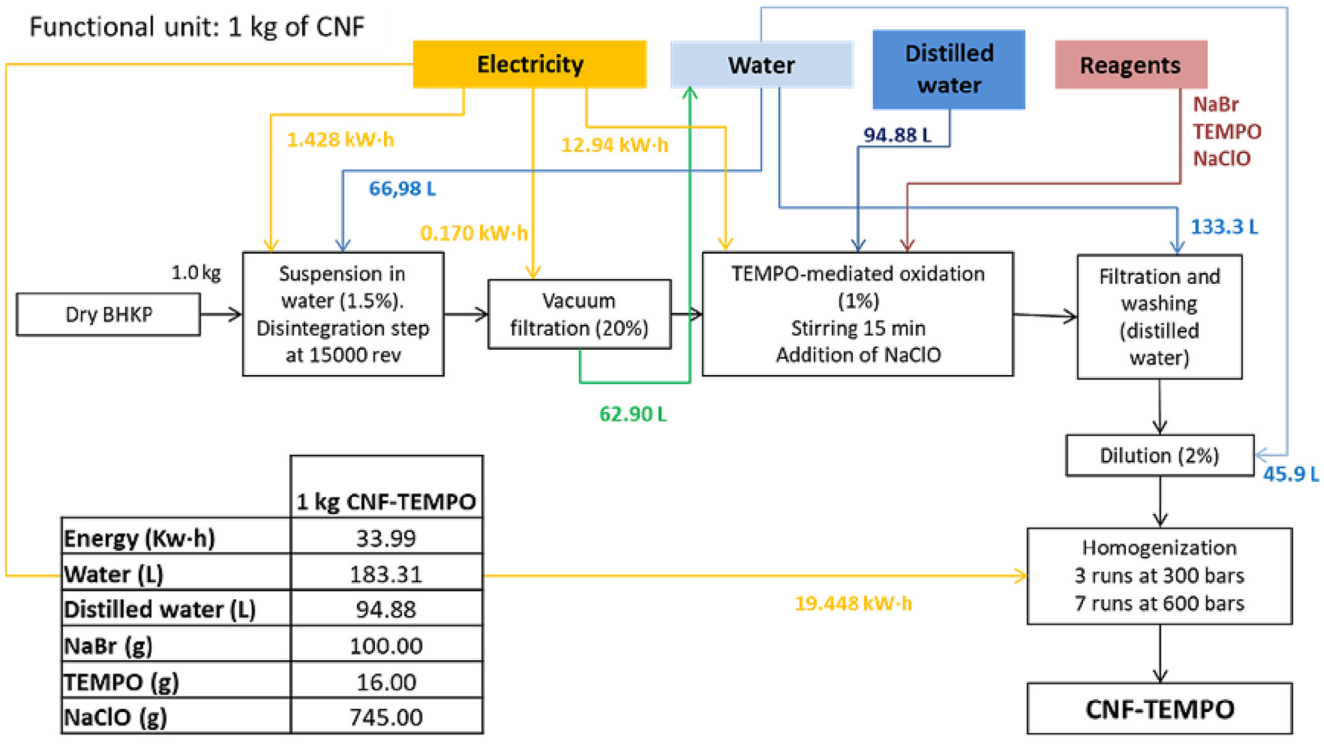


Fig. 4. Oxidation of the primary hydroxyl groups of cellulose, at pH 10, considering a TEMPO/NaBr/NaClO system (Carlsson et al., 2014).



	1 kg CNF-TEMPO
Energy (Kw·h)	33.99
Water (L)	183.31
Distilled water (L)	94.88
NaBr (g)	100.00
TEMPO (g)	16.00
NaClO (g)	745.00

Fig. 5. Process diagram of the TEMPO-mediated oxidation for the production of CNFs.

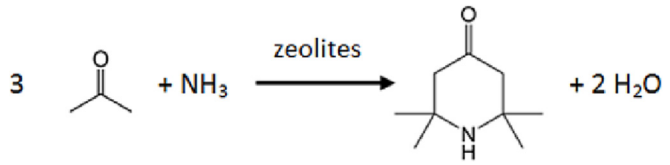


Fig. 6. Condensation of acetone and ammonia catalyzed by zeolites to produce triacetonamine (TAA).

bottoms comprise a high-boiling solvent (250 cm^3 or 279 g of triethylene glycol), paraffin oil (56.3 g) and an alkali metal hydroxide (42.1 g of KOH). The hydrazine is spontaneously cleaved under these conditions. In addition to the nitrogen released, a reaction mixture comprising TEMPO, water and hydrazine is distilled off. The condensation product formed two phases, which are separated. The organic phase contains 91 % of TEMPO having >99 % purity.

Different works have described techniques for the last step of oxidation of TEMP, using hydrogen peroxide-sodium tungstate systems (Rozantsev and Sholle, 1992), hydrogen peroxide in absence of tungstate (Winter and Malherbe, 1989), or electrochemical techniques (Kagan et al., 2011). Hydrogen peroxide is used as an oxidizing agent to synthesize TEMPO using a multi-necked flask, equipped with a propeller agitator, reflux condenser, dropping funnel and pH electrode. 28.25 g of TEMP are mixed with 46 mL of methanol and 4.07 mg of $MgCl_2{\cdot}6H_2O$, previously dissolved in 1 mL of water. TEMP, methanol, and the magnesium chloride solution are heated to 65 °C. Then, over 45 min, 45.3 g of a 30 % aqueous H_2O_2 solution are added dropwise and stirred for 7 h at 65 °C. The evolution of the reaction can be monitored via gas chromatography analysis. To purify the TEMPO, 5 mL of 10 % sulfuric acid is added, and the reaction mixture is extracted four times with 50 mL of cyclohexane. The cyclohexane is removed by distillation, and the final yield of this synthesis route is 85.5 %.

4. Life cycle assessment

4.1. Functional unit and system boundaries

Since the three CNFs have different morphologies, their LCA values should not be compared directly. The energy consumptions might vary depending on their degrees of nano-fibrillation or conditions of mechanical treatment in water. However, there is no suitable standard method at present to accurately determine the degrees of nano-fibrillation of CNFs, and thus it is not possible to prepare CNFs with the same degrees of nano-fibrillation or the same CNF morphologies for comparison of their LCA values.

Therefore, the yield of fibrillation – that provides the mass fraction of nanosized objects in the CNF suspension – of each type of CNF (TEMPO-oxidized, enzymatic, and mechanical), and SEM images showing the morphological differences between them are presented in Fig. 8.

Yield of fibrillation was determined by centrifuging a diluted CNF suspension (0.2 wt%). The nanofibrillated fraction, contained in the supernatant, was isolated from the non-nanofibrillated, which was assumed to get retained in the sediment. The recovered sediment was oven-dried until constant weight and referred to the initial dry mass, obtaining the non-nanofibrillated fraction. The nanofibrillated fraction was calculated by difference.

TEMPO-oxidized CNFs exhibited an entangled 3D-structured network of nano-sized fibrils. In addition, the surface of the obtained CNFs appeared to be smooth and without excessive surface fibrillation, which is attributed to the effect of carboxyl groups during fibrillation, which contributed to fiber disruption. In the case of enzymatically hydrolyzed CNFs, the surface also was found to be smooth and with no significant surface fibrillation, but diameters were considerably bigger than in the case of TEMPO-oxidized CNFs. Finally, in the case of mechanically obtained CNFs, the surface fibrillation of the CNFs became apparent, as well as their bigger size, with some fibers in the microscale, rather than in the nanoscale. The absence of functional groups that may contribute to fibrillation (as in the case of carboxyl

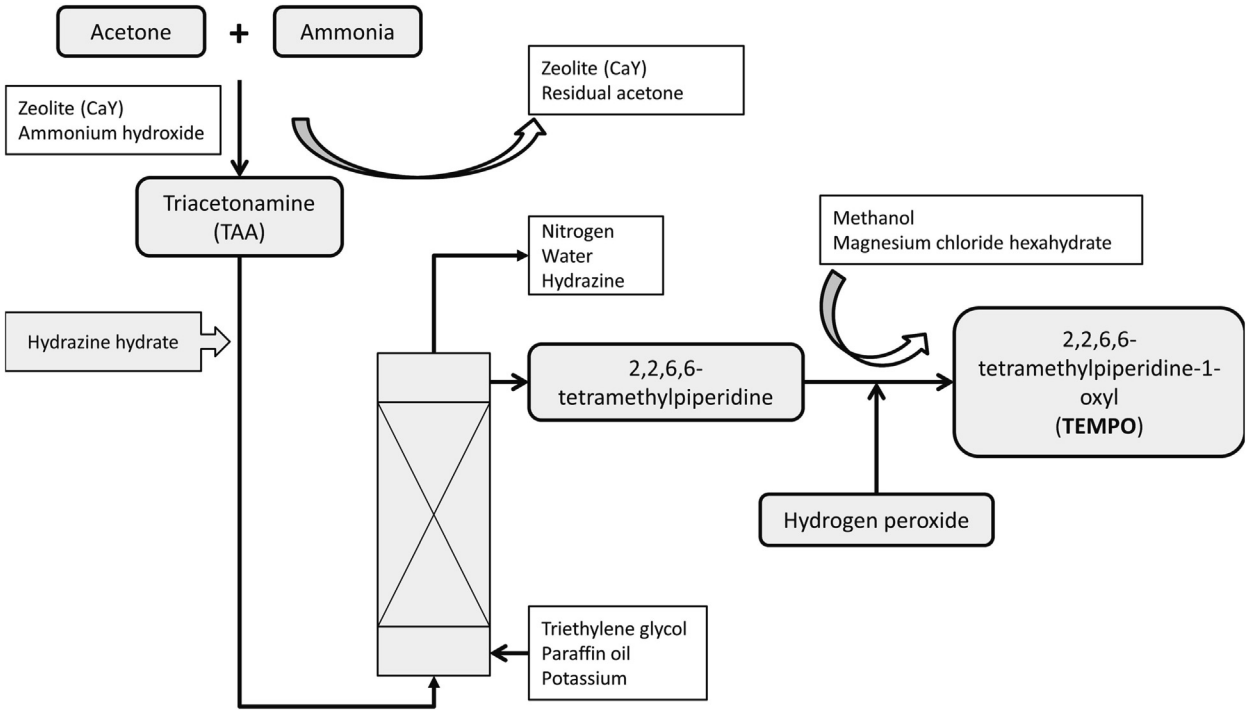


Fig. 7. Process diagram of the TEMPO production route (Winter and Malherbe, 1989; Rozantsev and Sholle, 1992; Kampmann and Stuhlmuller, 1997; Maltz et al., 2002; Cao et al., 2010; Kagan et al., 2011; Gliozzi et al., 2014).

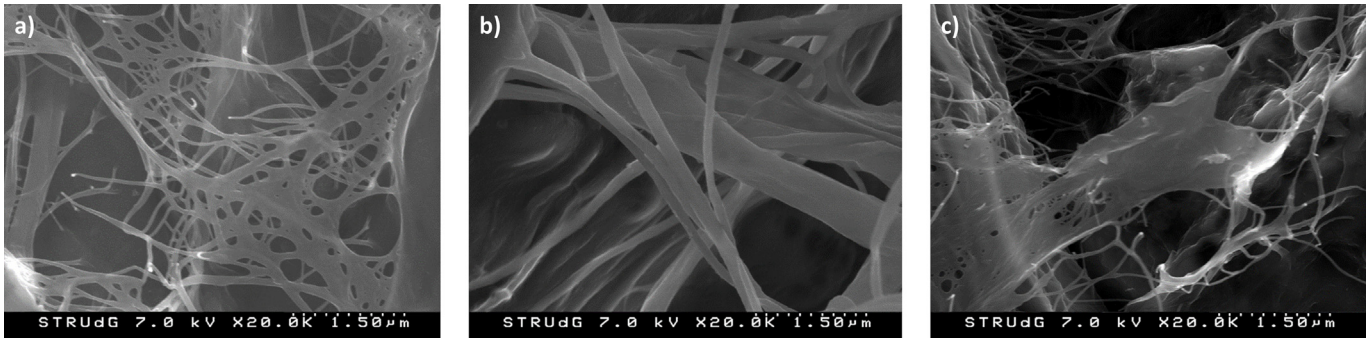


Fig. 8. Morphological differences between: a) TEMPO-oxidized CNF (yield of fibrillation ≥ 95 %); b) Enzymatic CNF (yield of fibrillation = 39 %); and c) Mechanical CNF (yield of fibrillation = 21 %).

groups) or the use of enzymes for shortening the cellulose chain, the effect of the high-pressure homogenizer was found to be much more aggressive, leading to a higher heterogeneity on the size distribution and, in addition, to a higher branching of the obtained CNFs.

The functional unit chosen is not centered solely on the amount of CNFs produced, given that the three pre-treatments considered result in products of different nature. To our judgment, it is sensible to define the functional unit with regards to their purpose. In the context of paper strengthening, by means of bulk addition as described above, the following improvements in comparison with the no-CNFs-addition case:

- TEMPO-oxidized CNFs: 101 % of tensile strength increase;
- enzymatic CNFs: 103 % of tensile strength increase;
- mechanical CNFs: 71 % of tensile strength increase.

Taking into account that the range of tensile strength variations is linear up to additions of 6 % CNFs (González et al., 2012), to achieve the same increases as the enzymatic route, in weight percentage, TEMPO-oxidized CNFs should be added at 3.06 % and mechanical CNFs at 4.35 %.

Therefore, the functional unit will be corrected to 1.02 kg of TEMPO-CNFs, 1.00 kg of enzymatic CNFs and 1.45 kg of mechanical CNFs. Consistently with this approach, these numbers would vary should the purpose of the nanocellulosic materials differ from paper strengthening.

The analysis includes the extraction of the raw materials, chemicals, and energy as well as the processing of CNFs following the three different routes, but it does not take into consideration the final use or disposal phase of the CNFs obtained (therefore, a cradle-to-gate scope is taken). Industrially, the requirement of high-pressure homogenization is usually avoided since it consumes a high amount of energy. However, we compare the processes in the laboratory conditions where this stage is used. Since we are considering the same conditions in the homogenization stage of all the pretreatments, this does not affect the LCA conclusions.

The end-of-life stage is not considered to be relevant for the study because CNF waste management would not depend on the technology used to produce it (Fig. 9).

4.2. Life cycle impact assessment of the three technologies

Like most nanomaterials, the production of CNFs is, albeit rapidly evolving, still in an early stage of technological development, in which lab-scale processes with high consumption of energy and materials are employed. When scaling to an industrial level, recycling, energy integration and further optimization stages are implemented. This material and energy reduction is estimated at 20 % approximately, according to multiple publications (Piccinno et al., 2016; Morales-Gonzalez et al., 2019).

The LCIA is calculated from the LCIs of the processes depicted in Figs. 2, 3 and 5. The results show that the environmental impacts associated to the mechanical pre-treatment are slightly lower than the environmental impacts of the TEMPO-mediated oxidation pre-treatment. In turn, both the mechanical and the TEMPO-mediated oxidation pre-treatments have much lower impacts than the enzymatic pre-treatment for most of the PEF midpoint indicators. It can be pointed out that alternative enzymatic processes with high consistency are expected to exert a lower environmental impact that the one estimated in this work (Pere et al., 2020). Nonetheless, the same can be said of other pre-treatments for nanofibrillation, including high-consistency oxidation, kneading or extrusion (Tardy et al., 2021).

Fig. 10 shows the results for some of the indicators assessed (acidification, climate change, eutrophication, land use and photochemical ozone formation), corresponding to the same environmental indicators evaluated in the above-cited Novozym 476 LCA (Cheung et al., 2012). This has been calculated as a percentage of the environmental impact of each process normalized to the highest impact value, corresponding in all cases to the enzymatic pre-treatment.

4.3. Electricity mix projection

The projection of the European electricity mix in the next decades (2030 and 2050) (Capros et al., 2016) does not present any change in the tendency presented in the results of the LCA. Fig. 11 presents this projection, quantifying the environmental impact of each midpoint indicator as a

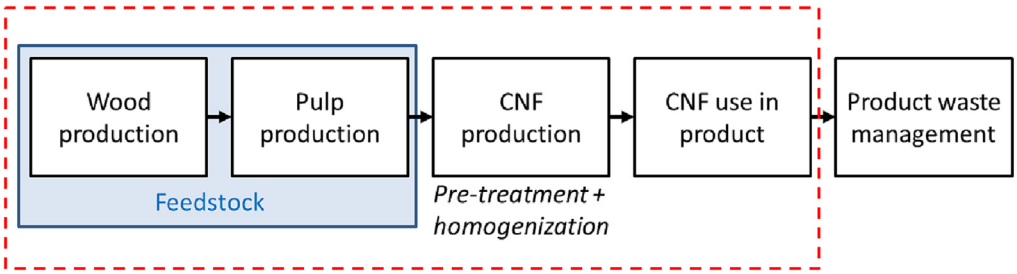


Fig. 9. System boundaries of the study.

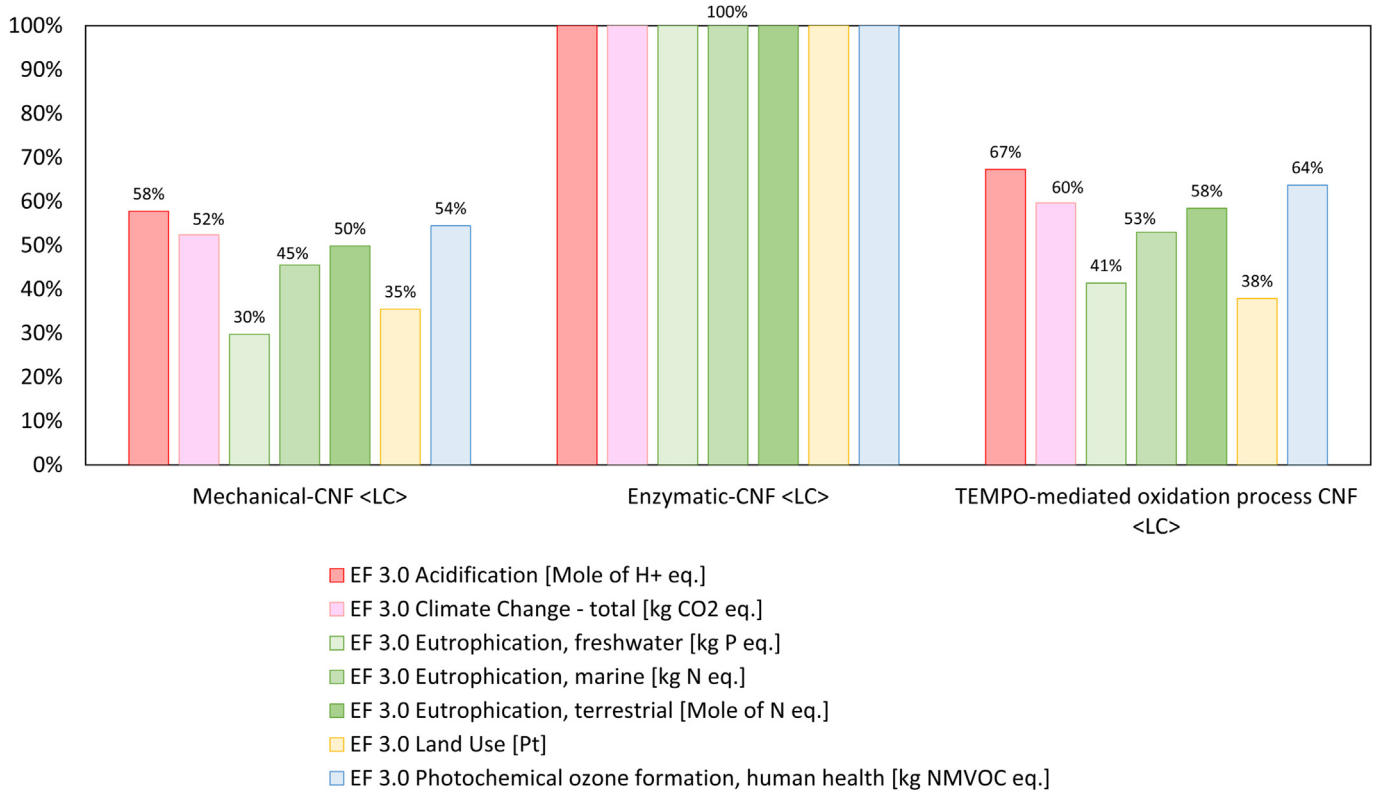


Fig. 10. LCIA midpoint indicators (PEF) of the mechanical, enzymatic and TEMPO processes.

percentage with respect to the highest impact value. Even though the state of affairs in the European Union at the time of finishing this study invites to disbelief, we could expect the same qualitative trend when comparing mechanical and oxidative pre-treatments to the enzymatic one. Considering that the three processes are fed with electricity as main energy source, they would be similarly affected by modifications in the electricity mix. Assuming an evolution of the electricity mix towards a greener mix, the impact associated with reagents and solvents will become more important. Which, in this sense, will be beneficial for the mechanical process.

5. Conclusions

The main finding of this life cycle assessment is that both mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. This confronts the truism or generalization that enzymatic processes are 'greener' alternatives to their chemical counterparts. Reasons for that are the need of a buffer solution for pH control, the temperature, and the time required (roughly, enzymatic > oxidative > mechanical). The conclusion stays the same when considering 1 kg CNFs as the functional unit and when correcting said functional unit on the basis of the required amount for a paper strengthening function. It is worth noting, however, that well-established conditions at laboratory level were assumed in all cases, and that these conventional conditions may differ significantly from the optimal ones.

Mechanical processes require fewer resources, nominally water and electricity. However, the physical properties of the product are worse (e.g., tensile strength), which means that a larger amount of CNFs must be produced to achieve similar properties to the CNFs obtained with the other pre-treatments. For this specific purpose, the TEMPO-mediated oxidation route achieves a product that, in terms of the required addition in

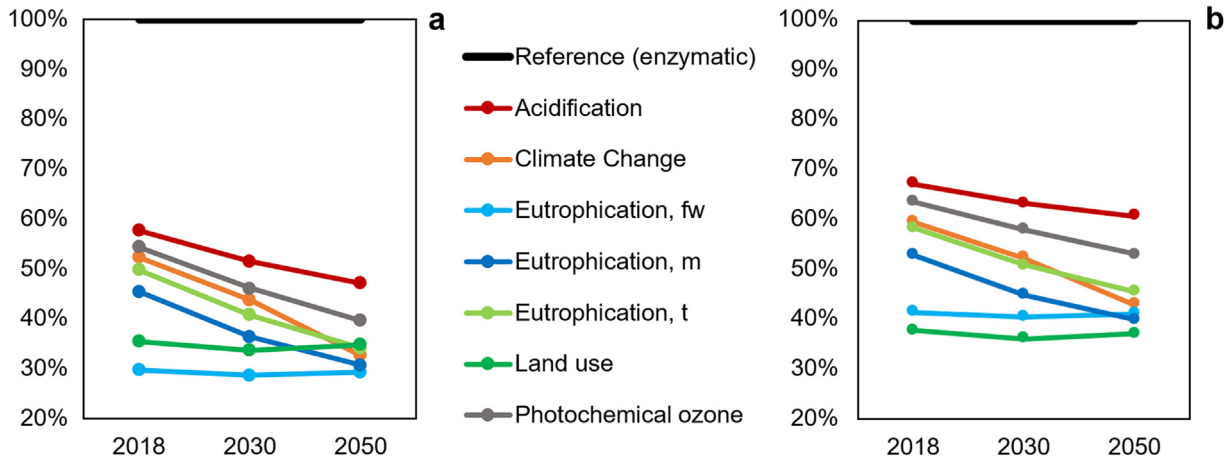


Fig. 11. Environmental indicators projection according to the European electricity mix evolution (2018–2030-2050). a: mechanical-CNF process b: TEMPO-mediated oxidation. *fw: freshwater; m: marine; t: terrestrial.*

papermaking to obtain sheets of similar tensile strength, matches the one produced via the enzymatic route.

Therefore, these factors should be considered when deciding which production route is the most appropriate, and this decision will depend on the quality required for the intended application of the final product.

Funding

No funding was received to assist with the preparation of this manuscript.

CRediT authorship contribution statement

All authors contributed to the study conception and design. Roberto Aguado, M. Àngels Pèlach, Quim Tarrés and Marc Delgado-Aguilar worked on the section "3. Modelling". They performed the experiments and provided technical knowledge on the chemical processes. Sergi Arfelis Espinosa, Didem Civancik, and Pere Fullana-i-Palmer worked on the section "4. Life cycle assessment" and provided technical knowledge on this methodology. The first draft of the manuscript was written by Sergi Arfelis Espinosa and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Sergi Arfelis: Formal analysis, Investigation, Data curation, Writing – original draft, Visualization **Roberto Aguado**: Formal analysis, Investigation, Data curation, Visualization, Writing – review & editing **Didem Civancik**: Formal analysis, Investigation, Data curation, Visualization **Pere Fullana-i-Palmer**: Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition **M. Àngles Pèlach**: Formal analysis, Investigation, Data curation, Visualization **Quim Tarrés**: Formal analysis, Investigation, Data curation, Visualization **Marc Delagado-Aguilar**: Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Acknowledgements

Authors wish to acknowledge the financial support of the Spanish Ministry of Science and Innovation to the projects CON-FUTURO-ES (PID2020-113850RB-C22) and VALORCON-NC (PDC2021-120964-C22). Marc Delgado-Aguilar and Quim Tarrés are Serra Húnter Fellows.

One of the authors, Sergi Arfelis would like to thank the UNESCO Chair in Life Cycle and Climate Change at ESCI-UPF for hosting the development of his PhD thesis on LCA of chemical reactions, of which the research presented in this paper forms a part, and the PhD programme in Environmental Engineering at the Universitat Politècnica de Catalunya, in which this thesis is registered. In addition, he thanks the start-up DEASYL SA, as his main source of funding.

The authors are responsible for the choice and presentation of information contained in this paper as well as for the opinions expressed therein, which are not necessarily those of UNESCO and do not commit to this Organization.

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