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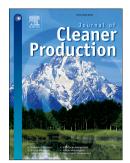
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Toward eco-efficient production of natural nanofibers from industrial residue: Eco-design and quality assessment

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Abstract

Conversion of bio-based industrial residues into high value-added products such as natural nanofibers is advantageous from an environmental and economic perspective, promoting resource efficiency along with the utilization of renewable materials. However, in order to employ the benefits of the raw material; its eco-efficient production should further be developed. Within this context, eco-design optimization through life cycle assessment (LCA) combined with life cycle costing (LCC) were applied to target eco-efficient production of natural nanofibers from carrot residue, along with quality assessment. The initial production steps included pretreatment combined mechanical nanofibrillation via ultrafine grinding, where the largest contributors to the environmental impact were identified as chemicals and energy. These were targeted by omitting the alkali pretreatment step and instead applying direct bleaching prior to nanofibrillation. After eco-design optimization, the yield increased while the energy, chemical, and water use significantly decreased. Therefore, a reduced environmental impact of more than 75% each for carbon footprint, freshwater ecotoxicity, and human toxicity was shown, along with a cost reduction of more than 50%. The use of carrot residue displayed an efficient conversion into natural nanofibers that was further promoted with the use of eco-design, yet with sustained functionality and nanoscaled dimensions, thus promoting resource-efficiency and natural nanofiber implementation in a wide range of promising bio-based applications.

Keywords: Cellulose nanofibers, Renewable resources, Energy efficiency, Sustainable production, Life cycle assessment, Life cycle costing

1. Introduction

Holistic understanding of nanomaterials and their production routes using system analysis tools is useful for the development of this emerging technology on an industrial scale. For natural materials, it is further essential to evaluate whether the low environmental impact that renewable resources offer is maintained when converting raw materials to nanomaterials. Eco-efficiency considers both the environmental impacts and costs across product life cycles, and has been recognized as a key component for achieving the climate targets of the European 2020 strategy (EPC, 2012). This applies to the entire chain of resources, from the sustainable use of raw materials to the reduction of waste (Huppes and Ishikawa, 2005).

The estimated sustainable availability of cellulosic biomass from residues in the EU was reported to be about 220 million tonnes per year, with an equivalent available quantity foreseen for 2030 (ICCT, 2013). The majority originates from crop residues, but also from waste from industrial processing, such as of paper and food, or forestry residues. However, it should be noted that some wastes and residues should be considered low-value input materials, while others may provide valuable environmental services. Natural nanofibers have previously been extracted from various types of industrial residues worldwide, such as orange peels (Hideno et al., 2014), carrot residue (Siqueira et al., 2016), hemp stems (Pacaphol and Aht-Ong, 2017), paper sludge (Adu et al., 2018), and wood waste (Bauli et al., 2019). The potential environmental benefits of natural nanofibers over existing fossil fuel-based materials are not only assigned to their renewable and abundant origin, but also connected to their potential uses. Their inherently high mechanical properties make them suitable as green reinforcements in lightweight structures (Kumode et al., 2017), which, combined with characteristics such as biocompatibility and biodegradability, offer an attractive material for applications such as biomedical material and

packaging (Rajinipriya et al., 2018). In addition, prospects for functionalization of the material have been exploited for wastewater treatment (WWT) membranes and for removal of bacteria (Hassan et al., 2017) and metal ions (Gasemloo et al., 2019).

Nanofibers are currently produced from bleached wood pulp, from which isolation can be performed by a variety of mechanical techniques, such as ultrafine grinding, high-pressure homogenization, or microfluidization (Rajinipriya et al., 2018). In addition, different pretreatments can be utilized before mechanical processes in order to facilitate the liberation of nanofibers, thereby reducing energy consumption, such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation (Delgado-Aguilar et al., 2015b), carboxymethylation (Arvidsson et al., 2015), and enzymatic pretreatment (Piccinno et al., 2015).

The production of natural nanofibers is beginning to be commercialized, and is still considered an immature technology in terms of the manufacturing readiness level (Gavankar et al., 2014) and regulations (Bergeson, 2013). For this reason, the extraction process by chemical and/or mechanical means is still associated with a relatively high energy demand and production cost, which are key obstacles for its use in a wide range of applications (Delgado-Aguilar et al., 2015a). Arvidsson et al. (2015) reported the possibilities of omitting pretreatment and its environmental impact, but with a higher energy demand for the mechanical treatment of wood pulp as a trade-off. By excluding pretreatment, the cost was significantly reduced; however, the overall environmental impact assessed through a life cycle assessment (LCA) was comparable.

Although considerable research has been devoted to exploring different means of achieving nanoscale materials, less attention has been paid to evaluating the production routes from a system perspective. Most of the studies focusing on the LCA of natural nanofibers have been limited to the laboratory scale with a high energy demand (Li et al., 2013; Piccinno et al., 2015).

Thus, economic assessment by life cycle costing (LCC) of production has not been the focus, although some examples can be found, namely studies by Delgado-Aguilar et al. (2015b) and Moon et al. (2017). Eco-efficiency assessment has essentially been overlooked as a tool in the sustainable technology development of natural nanofibers, apart from a recent study by Piccinno et al. (2018a) based on a scaled-up framework approach for industrial-scale production (Piccinno et al., 2018b).

In a previous study, we showed that carrot residue is a promising raw material for energyefficient production of nanofibers using the upscalable ultrafine grinding approach (Berglund et al., 2016). In this paper, systematic eco-design optimization of the carrot nanofiber production was performed at pilot scale, combined with economic assessment for promoted eco-efficiency through improved environmental performance, production- and resource efficiency.

The main motivation of this study was to gain a better understanding of the initial production process by identifying which steps in the process had the largest contribution to environmental burden. Subsequently, the processing route was optimized by omitting part of the pretreatment based on the eco-design feedback while assessing the effect on nanofiber characteristics. The comparative LCA and LCC of the initial and optimized processing routes showed how system analysis tools can contribute to improvement of production processes by reducing the steps with the highest environmental impact, thereby promoting the development of eco-efficient production of nanofibers from industrial residues, in turn promoting sustainable technologies and products. Moreover, quality assessments of the nanofibers obtained from the two processing routes were compared in terms of their chemical compositions, network characteristics, and dimensions.

2. Materials and methods

2.1 Production of carrot nanofibers

2.1.1 Raw material

Carrot residue was supplied by Brämhults Juice AB (Brämhult, Sweden) as a by-product of carrot juice production.

2.1.2 Pretreatment

Pretreatment of the residue was initially conducted in three steps, in order to purify the cellulose, namely washing (W) with distilled water at 80 °C for 2 h, alkali treatment (A) using 2% NaOH at 80 °C for 2 h, and bleaching (B) with NaClO₂ (1.7%) in an acetate buffer at 80 °C for 2 h, following the procedure reported by Siqueira et al. (2016). This pretreatment was referred to as route WAB. The second (optimized) approach was direct bleaching (B) according to the method described above, which was denoted as route B in this study. After pretreatment, the materials were washed using a filter while rinsing thoroughly with water, and this was repeated three times until a neutral pH was reached. The solid recoveries were calculated as yields for input in the LCA analysis according to the following equation:

Yield % = $W_1/W_0 \times 100$ (Eq. 1)

where W_1 indicates the dry weight of the sample after the chemical treatment and W_0 indicates the initial dry weight of the residue.

2.1.3 Mechanical fibrillation

Mechanical fibrillation of the carrot pulp was conducted at a concentration of 2 wt.% after the pretreatment using a supermasscolloider 10" MKZA 10-20J 15 kW ultrafine friction grinder from Masuko Sangyo Co., Ltd. (Kawaguchi, Japan). The fibrillation was performed at pilot scale following the procedure reported in previous study for lab scale (Berglund et al., 2016). Fibrillation was conducted in contact mode directly after initial feeding, and was gradually adjusted to 90 µm (negative) by setting the position of the lower grinding stone to control the

clearance between the stones with a maintained rotor speed of 1500 rpm. Coarse silicon carbide grinding stones were used in this process, which are non-porous standard stones for soft materials. The pulp was subjected to compression and shear forces between the stones, which determined their output size. The energy consumption for mechanical separation was based on the direct measurement of power using a Carlo Gavazzi EM24 DIN power meter (Belluno, Italy) with a sampling frequency of 5 min and the processing time. The cumulative energy demand integrated over the whole fibrillation time was calculated from the following equation:

Energy = power (W) \times time (h) (Eq. 2)

The energy consumption for the grinding process was expressed as kilowatt hours per kilogram of dry weight of nanofibers.

2.2 Quality assessment

In order to assess the degree of fibrillation, samples were collected at regular intervals during the fibrillation process and characterized through viscosity measurements following the procedure reported in a previous study (Berglund et al., 2016). The process was finalized when a plateau in viscosity was reached, that indicated a strong gel formation of separated nanofibers (Berglund et al., 2016), and no larger structures could be detected by an optical microscope. The sugar composition analysis of the raw material (carrot residue) and the materials processed via routes WAB and B were characterized. The monosaccharide composition was determined using acid methanolysis followed by gas chromatography analysis. Sulfuric acid hydrolysis followed by high-performance liquid chromatography analysis was used to detect cellulose (as glucose). Methanolysis and gas chromatography-flame ionization detection analysis were performed according to the method described by Willför et al. (2009) using a HP 6890 series GC system and DB-1 capillary column (Agilent Technologies, Santa Clara, USA). Meanwhile, acid

hydrolysis was used to detect cellulose (as glucose); both methods were performed in triplicate. Briefly, approximately 20 mg of freeze-dried samples was weighed in Kimax tubes and 250 μ L of 72% sulfuric acid was added to each tube. The samples were pre-hydrolyzed at 30 °C for 1 h in a water bath and then diluted with 7 mL of MilliQ water. The samples were then incubated in an autoclave for 1 h at 121 °C and 15 psi. The samples were filtered with 0.45 μ m GH Polypro filters and diluted with MilliQ water before analysis by high-performance anion-exchange chromatography with pulse amperometric detection. The monosaccharides and uronic acids were separated in a CarboPac PA1 column (250 mm × 4 mm i.d.) or PA-10 column (250 mm × 4 mm i.d.) (Dionex, Sunnyvale, CA) and were detected using a 2465 pulsed amperometric detector (Waters, USA). The monosaccharide and uronic acid contents were determined based on external standards.

Atomic force microscopy (AFM) was used to measure the dimensions (widths) of the WAB and B nanofibers. The suspensions (0.01 wt.%) were dispersed and deposited by spin coating onto a clean mica for imaging with a Veeco Multimode Scanning Probe (Santa Barbara, USA) in tapping mode with a tip model TESPA (antimony (n) doped Si) (Bruker, Camarillo, USA). The measurements from the height images were conducted in air at 23 °C using Nanoscope V software. The average values and deviations presented were based on 50 different measurements.

The mechanical properties of the dried nanofiber networks were studied as an indication of the degree of fibrillation, where an increase in mechanical properties have been associated with the fibrillation process (Adu et al., 2018). Nanofiber networks were prepared using vacuumassisted filtration, and were dried, dimensioned, and conditioned according to a previously reported procedure (Berglund et al., 2016) prior to tensile testing. The density of the networks was calculated using a gravimetric method; an analytic balance was used to determine the weight

and a micrometer gauge was used to measure the thickness based on an average of 10 different measurements per material. The average tensile testing results were based on at least 10 sets of measurements for each material.

The wettability of the nanofiber networks was characterized using water contact angle measurements with an EASYDROP measuring system, drop shape analysis control (DSA1), and evaluation software (Krüss GmbH, Hamburg, Germany) according to the procedure reported by Berglund et al. (2017). A 4 μ l water drop was placed onto the samples, and the contact angle was calculated using the sessile drop technique. The reported values were the average of five measurements for each sample.

Moreover, the topographical features of the nanofiber networks were studied using the same AFM setup described above, and the root mean square roughness was calculated to study its contribution to the wettability measurement (Berglund et al., 2017). The reported values were the average of five measurements on a surface area of 25 μ m².

2.3 Life cycle assessment

The LCA used in this study was conducted according to the International Reference Life Cycle Data System (ILCD) Handbook including the ILCD 2011 Midpoint+ method for life cycle impact assessment (LCIA) (EC, 2011) and the ISO standards on LCA (ISO 14040, 2006; ISO 14044, 2006). Furthermore, the LCA calculations were performed using LCA software SimaPro 8.3 (PRé Consultants, the Netherlands, 2016).

2.3.1 Goal and scope of the life cycle assessment study

The overall aim of LCA is to compare the full range of environmental effects assignable to products and services by quantifying all inputs and outputs of material flows and assessing how these affect the environment. The first phase of the LCA study was to define the goal and scope,

which in the present study was the evaluation of the environmental impacts for the production of carrot nanofibers by means of chemical pretreatment and mechanical fibrillation using carrot residues as the raw material. Based on this, the aim was to show how eco-design could be applied to optimize the environmental performance of production through identification of environmental hotspots, and to perform a comparative LCA on the two processing routes. The LCA was performed at a pilot scale in order to provide eco-design feedback and environmental performance suitable for industrial uses. Thus, the intended audience of the study was primarily researchers and companies that work with these materials; however, it was also anticipated to interest a broader audience, including policy makers.

The functional unit and system boundaries were defined as 1 kg of 2 wt.% carrot nanofiber suspension, which corresponded to a dry weight of 20 g. The LCA analysis was conducted "from cradle to gate." The system boundaries, which could be divided between the foreground and background system, included the production and transport of input materials, energy and water consumption during manufacturing, and waste and WWT. Infrastructure was excluded, except in the case of database processes already containing infrastructure.

The time and geographic boundaries referred to primary data from 2017. Secondary data originated from the Ecoinvent v3.3 database (Ecoinvent Centre, 2016). Electricity mixes were country specific, or, if available, supplier specific. In general, the European situation was taken as a geographical reference.

The modeling approach was adopted in terms of attributional modeling since the main objectives of the analysis were identification of environmental hotspots and process optimization (eco-design). During the modeling of the life cycle of carrot nanofiber production, no specific multi-output allocation issues occurred. Concerning end-of-life allocation, the "cut-off" approach

was applied as a default. With this approach, outputs subject to recycling were considered inputs to the next life cycle, and no environmental burdens or environmental gains derived from the recycling process were allocated to the waste stream. Waste collection and transport to the recycling facility were included. In the case of carrot residues, this meant that the carrot residues were free of any environmental burden; however, the transport of carrot residues was included in the analysis. This assumption was further analyzed in the sensitivity analysis by means of economic allocation.

2.3.2 Inventory analysis

The second phase of the LCA study was the inventory analysis, which involved data collection and calculation procedures to quantify relevant inputs and outputs of the product system. There were two main sources of data; primary data referred to the original pilot-scale data, and secondary data or background data were derived from the Ecoinvent database (Ecoinvent Centre, 2016) and referred to the industrial scale. This LCA considered two production routes for carrot nanofibers. The first was production using route WAB prior to fibrillation, which, after ecodesign feedback, motivated the pursuit of production route B before mechanical fibrillation. The amount of chemicals, yields, water consumption, and energy consumption required for producing the functional unit of 20 g of carrot nanofiber for each production route are specified in Table 1.

Table 1. Input in terms of materials (dry weight), chemicals, water consumption, and energy consumption for both production routes, namely WAB (washing, alkali, bleaching) and B (bleaching), following mechanical fibrillation expressed by functional unit (20 g dry weight).

	Route WAB	Route B	Unit
Carrot residue	62.5	30.8	g
Pretreated pulp	20.0	20.0	g
Yield	32.0	65.0	%

Sodium hydroxide	19.8	2.1	g
Sodium chlorite	2.7	1.3	g
Acetic acid	12.3	6.1	g
Water (pretreatment)	8.5	1.5	kg
Energy (pretreatment)	0.29	0.05	kWh
Energy (mechanical)	0.02	0.01	kWh

The key inventory data per functional unit are shown in Table 1, and detailed input-output data are provided in Table S1 for route WAB and Table S2 for route B. The applied Ecoinvent processes selected for the LCA model for the chemicals, water, energy, and waste are provided in Table S3.

The electricity mix was country specific, and was represented by the medium voltage European electricity mix (Ecoinvent Centre, 2016). The choice of the electricity mix was further analyzed in the sensitivity analysis, which changed the European electricity mix to German, Belgian, and Swedish.

Transport distances for the carrot residue and chemicals were estimated with the freight represented by a truck (> 32 t) (Ecoinvent Centre, 2016). For the transport of the carrot residue from the carrot juice producer to production site, a middle-long distance was assumed (500 km). Generally, chemicals are available at the regional scale, and thus a short-middle distance was assumed (300 km).

The waste flows during the carrot nanofiber production processes were assumed to be treated by means of WWT plants with an average European wastewater capacity.

2.4 Life cycle costing and eco-efficiency

LCA and LCC were applied in parallel with the aim to evaluate the environmental impacts together with the economic aspects associated with the development of a suitable technology to produce nanofibers in order to determine techno-economically viable solutions and production methods. LCC is an economic analysis tool that includes all types of costs related to a product or process over its life span and its methodology was specified by Hunkeler et al. (2006). Additionally, the metric eco-efficiency was elaborated according to Huppes and Ishikawa (2005) and the ISO standard (ISO 14045, 2012) in order to combine the LCA and LCC results and evaluate the eco-efficiency of each technology. The eco-efficiency metrics of the two carrot nanofiber production routes were illustrated using the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2013) method for LCA, and were subsequently plotted against the LCC results. Cost data used in the LCC of the production are reported in Table S4.

3. Results and discussion

3.1 Life cycle impact assessment

LCIA was the third phase of the LCA study, and aimed at evaluating the significance of potential environmental impacts using the inventory results. This process involved associating inventory data with specific environmental impact categories. The impact assessment methods used in the performed LCA were selected according to the ILCD handbook (EC, 2011). The ILCD was limited to nine impact categories containing the most relevant indicators, which still provided a broad perspective on the environmental and resource impacts of carrot nanofibers, namely climate change in terms of global warming potential (GWP) (biogenic CO_2 was excluded owing to the neutrality approach); particulate matter; acidification; freshwater ecotoxicity; land use; water resource depletion; mineral, fossil, and renewable resource depletion; human toxicity: cancer effects; and human toxicity: non-cancer effects. The IPCC method (IPCC, 2013) described in the ILCD handbook (EC, 2011) has been applied as an easily recognizable indicator, and was used in the flow diagrams illustrated in the inventory where a 100 year time horizon of GWP relative to CO_2 was considered.

The two processing routes were presented together to allow for comparison and to show how the impact assessment and identification of hotspots was conducted and how the optimization approach was chosen.

The quantification of the impact categories according to the ILCD 2011 Midpoint+ method (EC, 2011) is provided in Table S5 for both routes in relation to the production of 1 kg of 2 wt.% carrot nanofiber suspension in water. The impact of production route B was significantly reduced by at least a factor of 3 for all selected categories in comparison with that of route WAB (Table S5). The most considerable impact reduction was seen for the categories of carbon footprint (GWP), freshwater ecotoxicity, and human toxicity (non-cancer effects), which corresponded to a decreased environmental impact of more than 75%.

3.2 Interpretation

The fourth phase of the LCA consisted of interpretation of the results from inventory analysis and impact assessment in the light of the goal and scope definition. This phase was conducted by means of contribution analysis to identify the environmental hotspots, followed by quality assessment of the obtained nanofibers from both routes. Moreover, quality assessment, sensitivity analysis, and comparison with other studies were included in order to consider the limitations and draw conclusions and recommendations to apply in further process development.

3.2.1 Contribution analysis: Identification of environmental hotspots

In order to interpret the LCA results of the production routes, a contribution analysis was performed, which specified the largest contributors to the environmental burden in the different categories, as shown in Figure 1. Flow diagrams of the production are provided in Figures S1 and S2 for routes WAB and B, respectively. The GWP of production route WAB was assigned to contributions from the energy and chemicals (Figure 1), namely sodium hydroxide, acetic acid,

and sodium chlorite (Figure S1). Furthermore, these were the main contributors for a majority of the impact categories. A larger contribution from chemicals and water consumption was observed for the mineral, fossil, renewable, and water resource depletion, respectively (Figure 1). It was also seen that transport and WWT had the smallest contribution to the environmental impact. Based on the contribution analysis (Figure 1), the environmental hotspots were identified as the energy demand and chemicals. Accordingly, the approach for optimization of the production route was to target energy demand in combination with the chemicals used.

In a previous study, we showed that most of the yield was lost during the alkali step of the pretreatment of carrot residue prior to mechanical grinding (Berglund et al., 2016). In addition, Iwamoto et al. (2008), among others, reported the importance of hemicellulose for process efficiency of nanofibrillation of wood pulp using ultrafine grinding. The eco-design approach omitted the initial washing and alkali treatment step from route WAB and instead applied direct bleaching (route B) in order to reduce the contribution from chemicals. Furthermore, targeting the preservation of non-cellulosic components, such as hemicellulose and pectin, could in turn increase the yield and promote energy-efficient fibrillation, thereby lowering the contribution from electricity.

Table 1 shows that the yield more than doubled between route WAB (32%) and route B (65%), which consequently contributed to higher efficiency in terms of the use of chemicals, water, and energy, as observed from Figure 1. The most significant improvement in terms of energy efficiency was attributed to the reduced number of pretreatment steps requiring heat. Meanwhile, the energy demands of ultrafine grinding were comparable after eco-design optimization (Table 1). Still, for optimized route B, it should be noted that chemicals and

electricity were still the overall major contributors (Figure 1), thereby signifying an opportunity for further optimization.

3.2.2 Quality assessment

Quality assessment was conducted after eco-design optimization to evaluate the functional properties of the product at the end of the gate. The nanofiber characteristics are summarized in Table 2. Furthermore, the AFM characterization of the nanofiber widths dried from the gels and topography of the dried networks are shown in Figure 2.

Table 2. Nanofiber gel and dried network characteristics obtained after routes WAB (washing, alkali, bleaching) and B (bleaching). *The complete monosaccharides composition is shown in Table S6.

Gel		Glucose Non-o (mg/100 mg) (mg/		es Vi	iscosity nPa s)	Width (nm)
Route WAB	96.3*		10.9*	10	594 ± 28	10 ± 4
Route B	40.8*		39.9*	15	508 ± 16	12 ± 6
Dried network	E-modulus (GPa)	Strength (MPa)	Strain at break (%)	Density (kg/m ³)	Contact angle (°)	Roughness (nm)
Route WAB	12.2 ± 1.0	206 ± 10	5.5 ± 0.8	1.2 ± 0.04	71 ± 3	57 ± 10
Route B	14.0 ± 1.1	205 ± 12	1.8 ± 0.5	1.1 ± 0.03	55 ± 7	45 ± 9

The improved efficiency, which was partly owing to the higher yield of route B, was consequently attributed to the higher non-cellulosic content of hemicellulose and pectin, as confirmed from Table 2 and Table S6. The function of nanofibers as reinforcement will depend on several factors, such as the polymer that it is combined with, inherent properties of the nanofibers, and their dispersion, among others (Lee et al., 2014). In a previous study, we showed a promising reinforcing effect of carrot nanofibers on biopolyurethane foams using route WAB for the preparation of nanofibers (Zhou et al., 2016). Furthermore, Siqueira et al. (2016) reported the reinforcing capacity of carrot nanofibers using the same route in a cellulose acetate butyrate

polymer, as well as the redispersion ability of the nanofibers after drying. The ability for redispersion was shown to be further improved for sugar beets with an increased pectin and hemicellulose content (Hietala et al., 2017). The same study also reported that nanofibers containing pectin and hemicellulose displayed improved reinforcement, which was explained by better dispersion in the polyvinyl alcohol (PVA) matrix used in the study. The higher amount of pectin and hemicellulose obtained from route B may further promote redispersing features in combination with polymers, such as PVA, and thus further promote the use of environmentally benign constituents in industrial applications.

On the other hand, for orange peel waste, the importance of removal of non-cellulosic polysaccharides, such as pectin, covering the cellulose has been emphasized for the separation of nanofibers (Hideno et al., 2014). However, for carrot residue, the non-cellulosic polysaccharides did not seem to negatively affect the separation of nanofibers considering their measured width of below 14 nm (see Figure 2) and their strong and comparable network formation, which is reflected in the viscosity values in Table 3, for both routes. This was further supported by the mechanical properties of the nanofiber networks (Table 3) calculated from the stress and strain curves (Figure S3), which provided an indication of the degree of fibrillation in turn reflecting its reinforcing ability.

It is known that hemicelluloses are largely responsible for the tendency of cellulosic materials to swell in water (Laine and Stenius, 1997). Accordingly, the wettability toward water of cellulosic surfaces tends to decrease upon the removal of hemicellulose (Hosseinaei et al., 2011). This was in agreement with the contact angles measured for routes WAB and B (Figure S4; Table 2), where the latter displayed a significantly lower water contact angle. The differences in wetting were presumably assigned to the more hydrophilic behavior of the hemicellulose without

the contribution of surface roughness, which was comparable for both networks, as shown in Table 2 and Figure 2e) and f). The more hydrophilic nature of the nanofibers processed using route B could further add to the dispersion difficulties in non-aqueous mediums or polymers. On the other hand, they could also be more advantageously used in the preparation of membranes or hydrogels where a more hydrophilic behavior is beneficial.

3.2.3 Sensitivity analysis

Sensitivity analyses were performed to evaluate the sensitivity of two crucial assumptions in the goal and scope definition: the applied electricity mix and the allocation question of whether the carrot residue should be free of any burden or if some burden could be allocated to the residue by means of economic allocation for prospective production using route B.

In this LCA, the electricity mix was represented by the European mix since it was set as a geographical reference. In the sensitivity analysis, the electricity mix was changed to German, Belgian, and Swedish, as shown in Figure 3a). The sensitivity analysis showed that the choice of electricity mix, which was connected to the location of carrot nanofiber production, largely influenced the magnitude of environmental impacts. Clearly, a country with a green electricity mix would significantly benefit the environmental performance related to carrot nanofibers. This was explained by the large contribution of the electricity mix in the environmental burden of carrot nanofibers.

Staffas et al. (2013) described the concept of a bio-based economy, which uses bio-based resources rather than fossil-based products and systems, and further analyzed the strategies for this transition among different countries. Replacing the acknowledged limited fossil resources for energy, chemicals, and materials with biomass was identified as a major challenge for all countries in terms of availability. Accordingly, agriculture and forestry alone would not be

sufficient to replace the fossil-based carbon used today, which consequently requires research on materials from waste streams for use as raw material. Furthermore, the availability or scarcity of biomass must be addressed, in addition to its eco-efficient conversion.

Carrots are the second most popular vegetable globally after potatoes, with a worldwide production of 33.6 million metric tonnes (Bayón et al., 2018). About 30-40% of carrot pulp remains after the juice has been extracted, thereby providing a high potential global production of raw material with more than 60% fiber in the form of a by-product.

The second sensitivity analysis, as shown in Figure 3b), concerned the allocation question of whether the carrot residue should be free of any burden or if some burden can be allocated to the residue by means of economic allocation.

In the sensitivity analysis, a future value of carrot residues in relation to carrot juice was assumed. For the allocation of carrot cultivation to both products, economic allocation was applied based on a yield of 66.7% for carrot juice (Bayón et al., 2018) with an estimated value of $4.5 \notin/kg$ (Table S4). Consequently, a yield of 33.3% for carrot pulp was applied with an assumed value of $1.0 \notin/kg$ (Table S4). As a result, 90% of arrot cultivation was allocated to carrot juice, while 10% was allocated to carrot pulp. Although a major virtue of waste feedstock is its low cost, it can generally be acquired for the cost associated with the transport of the material (Brown, 2003), which is what the assumed value of carrot residue was free of any burden. The sensitivity analysis showed that the allocation choice concerning carrot cultivation resulted in a significant increase in environmental impacts. Once carrot residues obtain a market, and thus economic value, it is advised to use economic allocation in order to take carrot cultivation into account in the LCA.

3.2.4 Comparison with other studies

Table 3 shows the LCA study of the two routes in comparison with other technologies studied to extract nanomaterials, including different raw materials, pretreatments, and mechanical separation approaches.

Table 3. Comparison of our process with other life cycle assessment studies on different routes for nanomaterial production where the process energy demand and global warming potential (GWP) are expressed as per kilogram of nanomaterial (dry weight). *The energy demand refers to the consumption of the entire process, while the value in brackets only refers to the mechanical contribution. **The range covers a low-impact (unbleached sulfate pulp) and high-impact (chlorine-bleached sulfite pulp) scenario. ***The range includes the use of ethylene and methane as feedstock.

Raw material	Pretreatment	Mechanical treatment	Electricity mix (voltage)	Energy demand [mechanical]* (kWh/kg)	GWP (kg CO ₂ eq)
Carrot residue	WAB	Ultrafine grinder	EUR (med)	15.5 [0.9]	11.7
Carrot residue	B	Ultrafine grinder	EUR (med)	3.0 [0.7]	2.9
Carrot residue	В	Ultrafine grinder	SWE	3.0 [0.7]	1.5
Carrot residue	Enzymatic	High-pressure homogenizer	EUR (med)	200.0	110.0
Wood pulp	-	High-pressure homogenizer	SWE	66.7 [52.8]	1.2-2.4**
Wood pulp	Enzymatic	Microfluidizer	SWE	23.9 [5.8]	0.8-1.6**
Wood pulp	Carboxy- methylation	Microfluidizer	SWE	491.9 [5.8]	99.0 – 110.0**
Carbon		mbly for carbon r production	USA	1847.0-2608.0	500.0- 700.0***

Enzymatic pretreatment followed by high-pressure homogenization have previously been used for nanofiber production from carrot residue (Piccinno et al., 2015). Enzymes have been used as

a more environmentally friendly approach compared with bleaching, but the overall GWP was still about 37 times higher compared with that of route B, as shown in Table 3. The higher environmental impact was attributed to the longer pretreatment required for the enzymes (24 h), which caused a higher electricity demand for the pretreatment compared with that of the 2 h required for bleaching; the heat loss in the laboratory-scale process also caused lower efficiency, which added to the impact. However, in a following study, a scale-up framework was applied for the laboratory-scale production, which reflected the higher efficiencies of large-scale production (Piccinno et al., 2018b). The environmental impact from heat was shown to be negligible in an industrial scenario given the use of a more efficient and well-insulated reactor.

Furthermore, the results from this study were compared with previous LCA results where wood was the source of raw material for nanofiber production using a Swedish electricity mix (Arvidsson et al., 2015). Table 3 shows that the GWP for route B was comparable with that of wood pulp with and without enzymatic pretreatment after mechanical fibrillation, even though the energy demand was significantly lower for the former. On one hand, the industrial scenario of wood pulping used in the study included wood production and transport, which added to the higher carbon footprint. On the other hand, the maturity of the pulping technology showed production that has been developed over time, including energy production on-site, recovery cycles of chemicals, and internal WWT (Arvidsson et al., 2015), which were not considered in this study; if adapted for an industrial scenario, they would significantly lower the impact from both chemicals and energy, which are the main contributors of carrot nanofiber production. Notable for an industrial-scale technology is that the cooling water required for a continuous process of mechanical fibrillation using ultrafine grinding would be anticipated to significantly contribute to a higher impact on categories such as water resource depletion and carbon

footprint. The impact of the carboxymethylation route on the GWP was more than 65 times higher compared with that of route B. However, it should be noted that the negatively charged carboxymethyl groups introduced with the treatment offered functionalization, and thus alternative uses for the produced nanofibers. The use of wood pulp as a source for raw material is appealing from the perspective that it has already been purified and reduced to microsized fibers, and as such could be used as is with a nearly 100% yield compared with the lower yield of carrot residue (65%). Still, the comparable or higher GWP for these routes (Table 3), given the differences in pulping scenarios, signified that a greater effort is needed to disintegrate wood fibers into nanoscale materials compared with the parenchyma cell walls of carrot (Berglund et al., 2016).

Carbon nanofiber is an example of another nanomaterial that can be used as reinforcement in lightweight nanocomposites; however, as seen from Table 3, its GWP was considerably higher in relation to that of natural nanomaterials. This was attributed to the energy intensive processing required for maintaining the high decomposition temperature during production (Khanna et al., 2008), but it should be noted that for benzene as a feedstock type, the energy use was more than 50% lower, which in turn would reflect a lower GWP.

3.3 Life cycle costing and eco-efficiency

From an economic perspective, the life cycle costs for different categories of the two routes are illustrated in Figure 4a). Furthermore, the LCC results were combined with LCA to obtain the eco-efficiency results, which are presented in Figure 4b).

The life cycle cost of 1 kg of 2 wt.% carrot nanofiber suspension via route WAB was $0.90 \in$ compared with the life cycle cost via route B of $0.42 \in$ (Figure 4a), thereby displaying a cost reduction of about 50%. For route WAB, the main contributions were from the material costs

(e.g., chemicals), while for route B this portion was significantly reduced, and thus constituted about a third of the main contributions divided between labor and maintenance costs.

In order to place this approach of processing route in a larger context, comparison with a study evaluating different pretreatment approaches using high-pressure homogenization was conducted (Delgado-Aguilar, 2015b). Route B corresponded to a production cost of 21 \notin /kg of nanofiber, which could be compared with 2.2 \notin /kg to 13.7 \notin /kg for bleached and mechanically and enzymatically treated nanofibers, respectively. The study also reported a production cost using TEMPO of 175.4 \notin /kg to 205.7 \notin /kg; however, it should be noted that all the costs reported in the study were based on the prices of chemicals and energy alone, and did not include any costs for labor or maintenance.

The synergetic effects of environmental impacts and costs have previously been reported in terms of eco-efficient production of nanocellulose-spun yarn from carrot residue with a cost between $10 \notin kg$ and $22 \notin kg$ of spun yarn (Piccinnoet al., 2018b). Thus, this reflected the further potential of the raw material for competitive natural composite applications, as well as how eco-efficient improvement at the early development stage of a technology promotes its potential.

In Figure 4b), the data points were clearly separated, thereby representing a win-win situation for production route B in terms of both cost and environmental impacts. This was not surprising since the omission of pretreatment resulted in a reduction of the environmental impacts by a factor of 4 and cost reduction of more than a factor of 2.

4. Conclusions

The present study showed how eco-efficiency can be applied as a tool for sustainable development by minimizing environmental impact and increase production efficiency of natural

nanofibers. The eco-design was performed by omitting pretreatment steps to minimize the energy demand and chemical use that were identified as the main contributors to the environmental impact. After the eco-design optimization, the environmental impact significantly decreased (75%) in categories such as carbon footprint and fresh water ecotoxicity owing to an increased yield, while the energy, chemical, and water use significantly decreased. In turn, resulting in a significant cost reduction (50%). The nanofibers displayed maintained functional properties in terms of their dimensions and network characteristics after the optimization. However, a higher pectin and hemicellulose content, and thus more hydrophilic behavior, were observed, which might make the nanofibers more suitable in the preparation of hydrogel or in membrane applications.

Altogether, the use of carrot residue as a raw material combined with bleaching and ultrafine grinding technology offers a promising route for the industrial eco-efficient production of natural nanofibers. The main recommendation from this study was to use industrial residues for fibrillation of biomass into nanofibers, which has a reduced environmental impact and is an economically favorable approach. In addition, the ultrafine grinding technology demonstrated a fibrillation method with a low energy demand, thereby further promoting environmental performance. For future development, it would be of interest to conduct LCA studies that include nanofiber use and end-of-life, that is, studies with a cradle to-grave perspective. Within this context, comparison of natural nanofibers derived from different industrial residues would be of interest.

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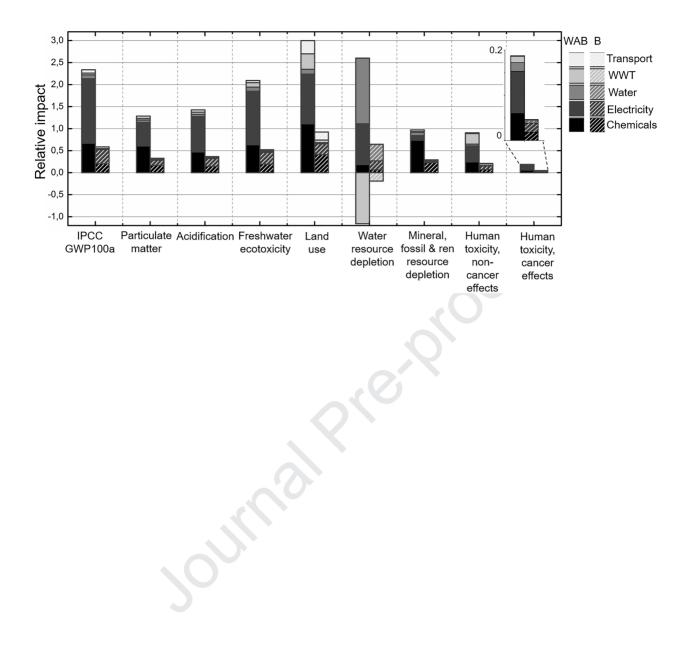
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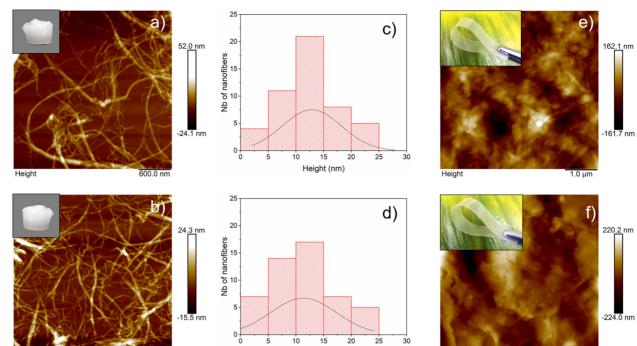
Figure 1. Relative impact based on the International Reference Life Cycle Data System (ILCD) (EC, 2011) and the corresponding contributions in absolute values for selected impact categories of carrot nanofiber production using route WAB (washing, alkali, bleaching) and route B (bleaching).

Figure 2. a), b) Atomic force microscopy (AFM) height images with insets of the gels; c), d) their width distributions measured from the height images; and e), f) the network prepared from the nanofibers from route WAB (washing, alkali, bleaching) and route B (bleaching), respectively.

Figure 3. Sensitivity analysis of the a) electricity mix of Europe, Germany, Belgium, and Sweden, and b) sensitivity analysis of the carrot allocation.

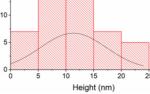
Figure 4. a) Life cycle costing (LCC) comparison specifying the different cost categories. b) Eco-efficiency results where LCC (\in) is a function of the life cycle assessment (LCA) (IPCC, 2013). *Transport costs are included in the material costs.





600.0 nm

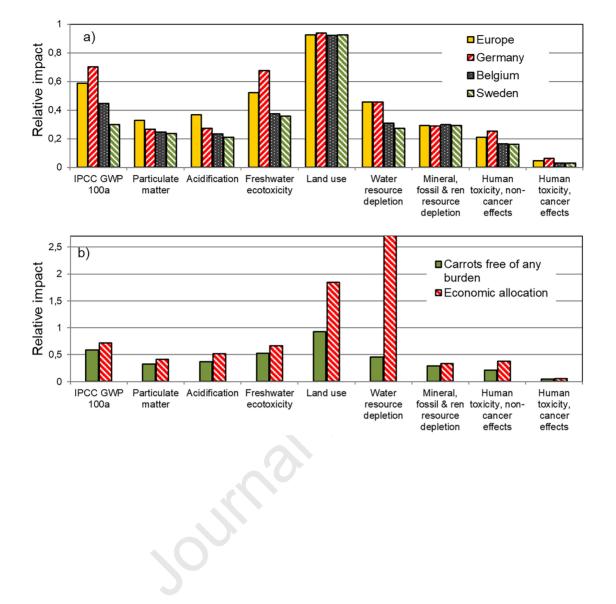
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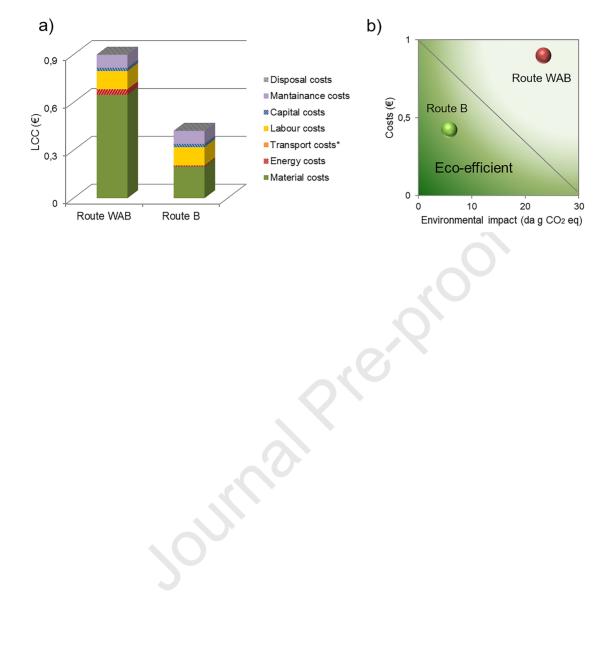


-224.0 nm

Height

1.0 µm





Highlights

- Eco-efficient production of high-quality natural nanofibers was demonstrated •
- Eco-design optimization via LCA resulted in a 75% reduction of the carbon-footprint •
- LCC revealed a 50% cost reduction after optimization of the processing route •
- Higher yield by preservation of hemicellulose and pectin enhances efficiency •
- An approach for efficient conversion combined waste minimization was presented •

Juna

Author statement

Linn Berglund: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization, Writing - Review & Editing **Leo Breedveld:** Conceptualization, Methodology, Investigation, Resources, Writing - Review & Editing **Kristiina Oksman**: Writing - Review & Editing, Supervision, Project administration

Journal Pre-proof

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Linn Berglund 215 Leo Breedveld Kristiina Oksman Smm (mm)