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Life Cycle Assessment of a New Technology To Extract, Functionalize and Orient Cellulose Nanofibers from Food Waste

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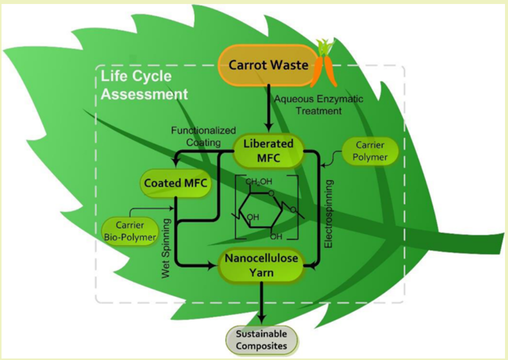
Supporting Information

ABSTRACT: A new technology for the production of cellulose nanofibers from vegetable food waste has been developed. The fibers are liberated enzymatically, given a functionalized coating and oriented using spinning techniques. We performed a laboratory-scale life cycle assessment (LCA) to assess the various routes of the entire production process from an environmental perspective. The results indicate that the electrospinning process has a higher impact than the alternative wet spinning process under the conditions described. Furthermore, to improve the liberation process of the microfibrillated cellulose, the enzymatic treatment step requires development; this could be through optimization of energy use in the heating process, mainly by reducing heat loss and water use. A comparative LCA with the results of other published studies, using different starting materials and chemical processes to obtain nanocellulose, provides a deeper understanding of our processes. From this comparison, we conclude that our technology has the potential to become a competitive alternative, outperforming other nanocellulose technologies from an environmental perspective.



KEYWORDS: *Nanocellulose, Life cycle assessment, Renewable resources, Sustainable chemistry, Sustainable innovation*

INTRODUCTION

Thanks to the continued growing interest in and pressure to manufacture sustainable products, numerous materials are being developed that are even expected to have a positive impact on the environment.[1,2] It is important to design, develop, appropriately evaluate and then improve production processes accordingly. Life cycle assessment (LCA) is one of the most important tools used to quantify the environmental impact of products or services. At early stages in development, especially for chemical processes, LCA can be useful for evaluating potential environmental impacts, to compare alternatives, identify hotspots, choose production routes and improve processes themselves.[3−5]

Cellulose nanofibers are derived from renewable resources, exhibit exceptional properties and are biodegradable at the end of their lives. They offer potential environmental benefits over existing materials such as carbon or glass fibers, helping to save materials and energy, substituting hazardous substances and using renewable resources. Nanocellulose is only just beginning to be commercialized and, therefore, most of the suitable fields for its application have still to be found. Nevertheless, this new material is attracting growing interest for a number of suggested applications ranging from food packaging because of its barrier properties, to medical applications or use in organic displays, thanks to its optical transparency:[6−9] several pilot and demonstration manufacturing plants have been built.[10] High tensile strength combined with low weight make nanocellulose an ideal candidate for the reinforcement of polymers, and their mechanical properties have been shown to exceed those of glass fiber reinforced plastics.[11] In our study, we used the multi-perspective application selection (MPAS) approach to make a first assessment of cellulose nanofibers based on technical, economic and environmental criteria.[12] This evaluated the potential for marketing cellulose nanofiber reinforced polymers as new materials and making successful products from them. The evaluation reported the most promising applications for cellulose nanofibers to be in luxury consumer goods such as high-end loudspeakers, in specialty vehicles (e.g., sidewalls for motorhomes), in industrial processing (e.g., marble protection during cutting and transport), and in furniture.

Materials made from renewable resources are often associated with being environmentally friendly. However, this is a simplistic conclusion and far from being correct in every case. For example, when agriculture is the source of a material, the fertilizers, pesticides and other chemicals used may result in a high environmental burden.[13,14] Furthermore, the impacts of the production process itself, the use and the disposal or recycling of the material have to be evaluated before any conclusion can be drawn. To obtain a product offering improved environmental performance, any of the above-mentioned life cycle stages can be addressed individually and, therefore, concentrating on the stage with the highest relative

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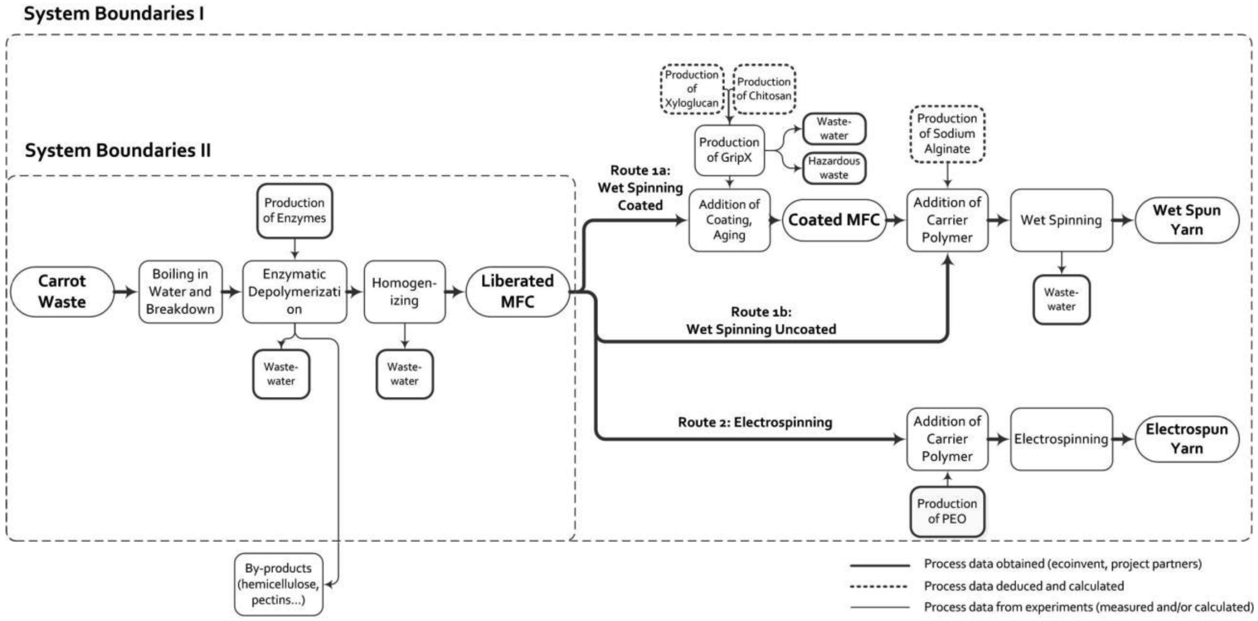

Figure 1. Production process and system boundaries for yarn spinning (I) and MFC liberation (II).

impact will most likely result in the greatest improvement. In the case of cellulose nanofibers, one approach is to use LCA in an attempt to improve a given material's production process while it is still in its developmental stage. Although improving the production process might only make a minor contribution to the end-product's overall environmental impact in comparison to its other life cycle phases (depending on the material's final commercial application), assessing and improving the production process at such an early stage makes good sense for a number of reasons. First, the development of the cellulose nanofiber production process is at a stage where possible future applications of cellulose nanofibers remain uncertain, making it difficult, if not impossible, to improve the material's environmental impact in its potential use and/or end-of-life phases (although that is where their highest relative environmental impact may emerge in certain applications). Second, carrying out an early LCA of the production phase allows for more flexibility; adaptions or changes can still be made with minor (financial) effort in comparison to a more mature stage of development. The opportunity to improve processes early on should be grasped. Such an improved environmentally friendly production process might also make sense from an economic perspective (especially in regard to energy and material efficiency and possible future regulations), lowering production costs in the short- and long-term and thus resulting in a more competitive product.

To the best of our knowledge, there are currently almost no available data on the environmental performance of cellulose nanofibers. Two studies have used LCA to evaluate the environmental impact of the laboratory-scale extraction of nanocellulose. Figueirêdo et al.[15] used white cotton and unripe coconut as the raw materials to produce cellulose nanowhiskers, and Li et al.[16] examined the production of microfibrillated cellulose (MFC) from wood pulp.

A recent research project developed a new aqueous-based process for extracting, functionalizing and orienting cellulose nanofibers from food waste, such as carrots. Due to the interesting mechanical properties of nanocellulose, the project focused on its use in reinforcing polymers in composite materials. The considerable differences between this new production method and other processes makes a comparison between them interesting. Using waste as a raw material immediately diminishes the production stage's environmental impact, as LCA does not have to account for the agricultural processes as long as the input is considered a waste from an upstream process.

This study used LCA to evaluate the above-mentioned cellulose nanofiber production process from waste materials. Because its aqueous-based process technology was still in an early developmental stage, only laboratory scale, experimental data were available and this is why a cradle-to-gate analysis was performed. The study's main goal was a better understanding of the overall production process. By detecting which steps in the process has the highest environmental impact and why (e.g., energy consumption, use of certain chemicals, etc.), the results can be used to improve the production process in the future. In a second step, we compared the LCA results of the aqueous-based process technology to other laboratory-scale LCA studies using different production methods and starting materials for making cellulose nanofibers. This comparison provides the process developers with a benchmark with which to evaluate their technology. Because the process was evaluated at the laboratory scale, the results are mostly used for qualitative conclusions.

■ MATERIALS AND METHODS

Goal and Scope. This study's overall goal was to carry out the first LCA of a newly developed process for extracting, functionalizing and orienting cellulose nanofibers from vegetable food waste. The system, shown in Figure 1, goes beyond the level of fibril extraction from the plant source and includes the coating and spinning of the MFC that results in a spun yarn. This form of MFC is optimized for use as a reinforcement for polymers (shown as System Boundary I in Figure 1).

The whole process was measured and examined at the laboratory scale. The data obtained came from a scaled-up laboratory procedure for testing purposes and measured the entire amount of MFC produced. For certain steps, energy consumption had to be estimated based on the equipment used. To facilitate this study's comparison

Table 1. Input and Output Values Used for the Different Processes

	liberated MFC	yarn route 1b	yarn route 1a	yarn route 2		GripX
inputs					inputs	
carrot waste [g]	100				chitosan [g]	1
electricity [kWh]	0.198	0.008	0.008	2.859	electricity [kWh]	0.138
tap water [kg]	0.032	0.037	0.036	0.012	xyloglucan [g]	0.015
enzymes [g]	0.160				DMSO [g]	2.751
MFC [g]		0.59	0.53	0.25	acetic acid [g]	0.027
sodium alginate [g]		0.72	0.65		H_2O [g]	0.25
acetone		0.21	0.19		EtOH [g]	3.945
GripX [g]			0.13		picoline borane [g]	0.000285
PEO [g]				1.4	cooling water [m^3]	0.003
other chemicals [g]		0.08	0.08	0.3		
outputs					outputs	
MFC [g]	1				GripX [g]	1
spun yarn [g]		1	1	1	hazardous waste [g]	6.973
wastewater [l]	0.201	0.054	0.052	0.004		
acetone into air [g]		0.21	0.19			

with previous publications on the production of nanocellulose, the production of 1 g of material (MFC or spun yarn) was chosen as the functional unit (FU). An FU based on target properties might seem more logical, but because this evaluation included no applications for the materials produced and previous case studies provided no data on mechanical properties, using the mass of material produced as the FU fitted with the comparative LCA. Because all the case studies obtained nanocellulose from plant sources, similar properties were to be expected. Scaling-up the procedure to an industrial level was evaluated. Because the process was at such an early stage in development, calculating a scaled-up LCA by simply using a scaling factor was not considered applicable. The equipment used in the laboratory process stage differed too much from any possible production plant, making a simple scale-up impractical and unrealistic. That technique might be applicable for simulating a large scale process once a more mature stage in development were reached, with a pilot plant built and its results quantified.[17,18] A framework was established to obtain logically derived LCA data by calculating and estimating the impact of laboratory-scale chemical production. Scaling-up an LCA is far from being a simple procedure and was beyond the scope of this study. However, in the future, this technique could be applied to the here presented cellulose nanofiber technology when comparisons with commercially available products (including other life cycle stages such as use and end-of-life) are assessed.[19]

The results of this LCA study help to evaluate the whole production process and highlight which steps are the main hotspots from an environmental perspective. Because the production process is not fully determined, there are competing options among the several production steps toward the desired outcome. A comparison of the LCA results therefore helps to indicate and choose the preferred production route from an environmental point of view. Because the technology examined is only at the laboratory scale, any comparison with potentially competing materials, such as carbon fibers or glass fibers, already produced at an industrial scale, would not yet be able to offer any meaningful results. Nevertheless, to obtain a better understanding of the newly developed process and how it performs, we compared our results to other LCAs of laboratory-scale nanocellulose production available from the literature. Cellulose nanofibers from different starting materials and production processes have previously been evaluated using LCA.[15,16] For comparison with other studies to be possible, the system boundaries need to be reduced to System Boundary II (as shown in Figure 1), i.e., to the sole process of liberating MFC. This is necessary as the comparison studies only focused on the liberation of MFC, which could potentially also be coated and spun into yarn. Additionally, to further improve the evaluation of this new technology's overall environmental performance by comparing the process only, regardless of location, the whole process was recalculated using the same electricity mixes as the other studies.

The raw materials in the laboratory process, which focuses on the proof of concept, are carrots. Although these particular carrots were not obtained from waste streams directly, the LCA study nevertheless treated them as such because the technology is being developed to produce material from a carrot-waste starting material. Other cellulosic source materials could potentially be used, and the enzymatic treatment step would have to be adapted according to their composition. Ideally, therefore, the input material should consist of a single, pure cellulosic source, and only industrial-sized vegetable waste streams match these requirements. Industrial carrot juice production seems to be an interesting line of investigation as a source of pure carrot waste in the form of pomace; carrot juice production has a low mass yield of 50%−70% (and thus produces a high proportion of waste) and is produced in large quantities.[20,21] Furthermore, the pomace has a much higher cellulose content (∼24 wt %) than the whole carrot (∼1−1.5 wt %).[22,23] To stay close to the laboratory experiments, we took the composition of the input material for the LCA study to be the whole carrot.

The possibility of including uncertainty calculations in the LCA was evaluated and rejected because the data were obtained from actual measurements and experiments in the laboratory. The data consisted of values for the entire amount produced and, in certain cases, estimations based on the equipment used. The experiments were not performed using several runs at this scale, thus it was impossible to obtain multiple experimental values and, therefore, a distribution of the measurements that allow a quantification of the uncertainty involved. Including the uncertainty of the measurements described here would require an assumption of the uncertainty distributions of the measurement techniques and equipment used. This would not have added value to the results, as the assumption itself would have contained uncertainty. Furthermore, this study's main goal was to evaluate and understand the production process at a laboratory scale where the relative contributions of the steps involved are more important than the absolute values. Those contributions were not expected to change significantly when uncertainty was included. This also means that the absolute results would deviate more due to the scale of production chosen than to the uncertainty of the measurements. The one uncertainty that it seems reasonable to include in this study is the handling of the starting material. Given that carrot waste could be used as biomass for energy production, as a fertilizer or in other applications, it can be argued that it should not be regarded as an input with no environmental burden. As biowastes become used in an increasing number of applications, competition for them could potentially make them products in their own right, of such economic value that there is an incentive to produce them. In that case, biowastes could no longer be regarded as burden free inputs. To

Table 2. Data Sources and Assumptions for the Various Process Steps

process step	input	remarks
whole process	electricity	Europe: electricity, medium voltage, production UCTE, at grid; *ecoinvent* v2.2 Brazil: electricity, low voltage, production BR, at grid; *ecoinvent* v2.2 US: electricity, production mix US; *ecoinvent* v2.2
whole process	waste treatment	treatment, sewage, to wastewater treatment, class 3, Switzerland; *ecoinvent* v2.2
whole process (except for GripX and carrier polymer production)	water	tap water, at user, Europe; *ecoinvent* v2.2
carrier polymer production	sodium alginate	production deduced according to refs 26−30, seaweed (not cultivated) as raw material, considered as *free* input
coating/adjuvant production	xyloglucan	production deduced according to ref 31, tamarind seed (waste) as raw material, considered as *free* input
coating/adjuvant production	chitosan	production deduced according to ref 32, crustacean shell (wastes) as raw material, considered as *free* input
coating/adjuvant production	hazardous waste	disposal, solvents mixture, to hazardous waste incineration plant, Switzerland; *ecoinvent* v2.2
addition of carrier polymer	production of ethylene oxide	ethylene oxide has been used instead of poly(ethylene oxide) (PEO); *ecoinvent* v2.2
coating/adjuvant production	picoline borane	generic average global dataset for organic chemicals used; *ecoinvent* v2.2
production of enzymes	whole process step	LCI results received from project partner
liberation of MFC	tap water	water input has been applied with 30% to reflect 70% recycling

reflect this uncertainty and understand the implications of the assumptions, we chose to include a scenario analysis for the comparative studies by accounting directly for carrot production. This scenario considered the carrots as being exclusively produced for the purpose of the nanocellulose production, meaning that 100% of the carrot production is allocated to this process. This reflected an extreme scenario giving carrot production the maximum possible impact, regardless of the allocation method chosen.

Life Cycle Inventory Analysis. The whole production process was split into the steps illustrated in Figure 1; the input and output values per FU are listed in Table 1. The starting material of food waste from carrots (15 kg per cycle) was put into about 15 L of boiling water for 1 h and then blended for 5 min. Next, the broken-down carrots underwent an enzymatic depolymerization process, during which the blend was exposed to a catalytic concentration of a specific enzyme mixture for 24 h at 40 °C. This liberated the cellulose from the rest of the carrot, which mainly consists of different polysaccharides such as hemicellulose and pectins. The enzymes were then inactivated by briefly raising the temperature. After filtration and washing with water, the liberated MFC (150 g dry weight) was resuspended in water and further broken down using a homogenizer. The separated polysaccharides were considered a byproduct that could potentially be used as the starting material for other production systems, and they were therefore set outside the system boundaries with no associated environmental burden or credit. Because no hazardous chemicals are involved in the liberation process, water can easily be recycled by filtering, which is why a recycling rate of 70% of the water is used. Once the liberated MFC was available, two different spinning methods, wet spinning (routes 1a and 1b in Figure 1) and electrospinning (route 2), were examined as alternatives for improving the orientation of the fibers.

In production route 1a, the MFC was is coated with a copolymer, GripX,[24] consisting of a primary amine functionalized chitosan backbone and xyloglucan side-chains. This coating was synthesized separately, added as an aqueous solution to the MFC suspension under stirring and left to age for 30 min. The wet spinning method was also examined without the coating (route 1b) to make the different spinning methods more comparable. An aqueous solution of sodium alginate (routes 1a and 1b) was added to the mixture and this acts as a carrier polymer for the subsequent wet spinning process. The spinning solution requires degassing for 1 h to prevent bubbles building up during the spinning process. The fibers are spun at a feed rate of 10 mL/min into a coagulation bath of calcium chloride and then a cold water bath for washing, before entering an acetone bath for solvent exchange. After drying at room temperature, the spun yarn is collected.

In the electrospinning case (route 2), poly(ethylene oxide) is used as the carrier polymer and added in aqueous solution. An appropriate electrospinning apparatus is used to spin and collect the yarn. Compared to the wet spinning process, the scale of production is considerably lower (feed rate of about 0.16 mL/min).

The specific energy and resource consumption for all these processes were measured or calculated based on the actual laboratory production protocol. A medium voltage, European electricity mix was chosen using the *ecoinvent* v2.2 database, which was the background data source for all available inputs.[25] Although the various steps in these process routes were performed in different institutions across Europe, transport between the various partners was not considered in this study. They were not necessary from the process point of view and would have distorted the results: we thus assumed that all parts of the processes occurred in one place. As the food-waste carrot raw material is a waste, the LCA considered it to be a free input. No data for picoline borane were available in the *ecoinvent* background database. In this case, *ecoinvent*'s generic average dataset for the production of organic chemicals was used as it was not expected to have a major impact given the very small relative quantity used (0.285 g per kg of GripX equated to 0.038 g per kg spun yarn). The production of other input materials, sodium alginate, xyloglucan and chitosan, derived from renewable resources, posed a greater challenge. An average dataset for organic chemicals would not have been appropriate, thus the respective production processes were modeled according to data available from different sources summarized in Table 2. More detailed descriptions of the inventory data for these biochemicals can be found in the Supporting Information.

The results of the present study were adapted to allow comparison with the other published studies on the extraction of cellulose nanofibers. One measure was the production process up to the liberation of fibers (i.e., system boundary II in Figure 1) as the two other studies only covered the liberation of MFC without further treatment. In order to compare the production process itself, and not its location, we also made an LCA of our process using Brazilian and American electricity mixes. The last measure for the comparative LCA was to also include the scenario with the carrot production.

Impact Assessment Methods. *ReCiPe* is one of the most up-to-date LCIA methods, valid for European conditions and thus very well suited for the present study. To evaluate the production process itself and try to improve it, *ReCiPe* midpoint and endpoint indicators were used taking the hierarchist perspective (the consensus, default model), as was cumulative energy demand (CED).[33,34] Assessing results at the midpoint and endpoint levels gives a more comprehensive view.

To compare, in the second part of this study, the results from the other studies, we also used the *Eco-indicator 99* method and the *IPCC*

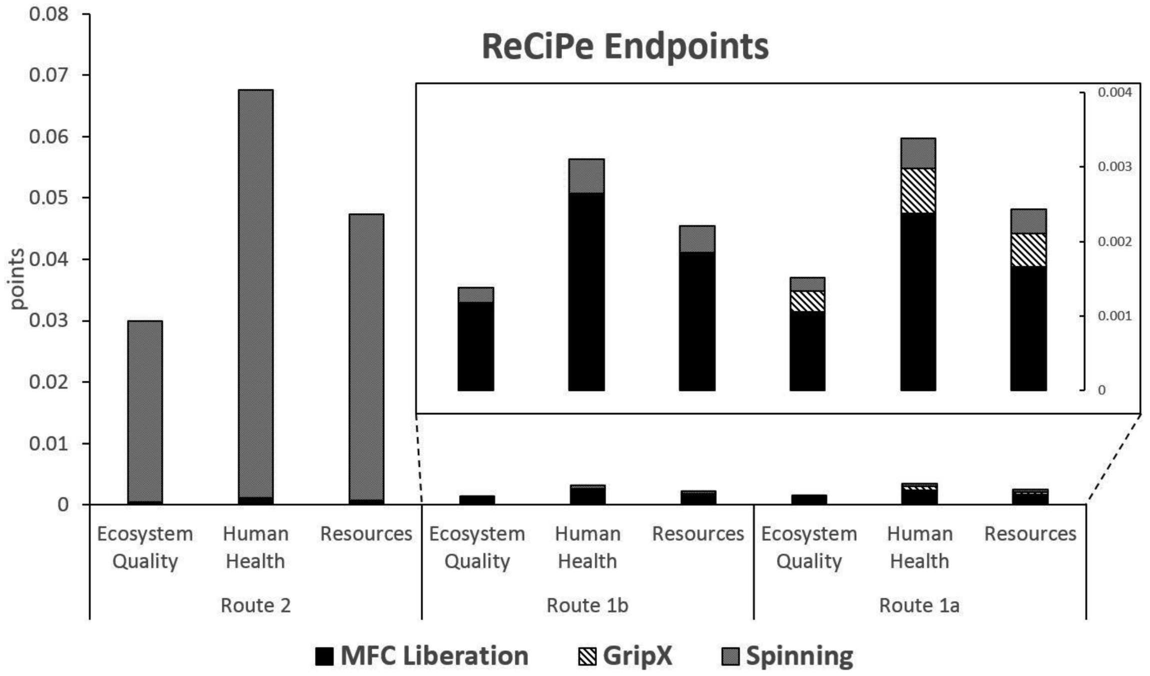

Figure 2. *ReCiPe* endpoint indicators for the production of 1 g spun yarn using different routes: 1a, wet spinning with coating; 1b, wet spinning without coating; 2, electrospinning.

2007 Global Warming Potential, the two LCIA methods applied in those other studies.[35,36] All the calculations of LCI data and subsequent LCIA results were made using OpenLCA (version 1.3.0) and the integrated *ecoinvent* version v2.2[25] database.

■ RESULTS

Life Cycle Assessment of the New Technology Developed. A comparison of the results for the three different production routes to the spun yarn showed that there was a huge difference between the two wet-spinning routes and the electrospinning route (see Figure 2). This difference resulted partly from the smaller scale of the electrospinning process, partly from the lower yield (60%) between the feed solution and the spun yarn, but mainly from the high energy consumption of the electrospinning apparatus. Electricity consumption during the electrospinning step accounted for 97.80% of the impact, as assessed using the *ReCiPe* endpoint (total) indicator (not shown). The same pattern was recognizable when the routes were analyzed at the midpoint level. This implies that the electrospinning process could only be competitive if larger-scale production reduced average energy consumption and material losses.

The wet-spinning process consumed significantly less energy. The liberation of the MFC was identified as the significant step along this route, accounting for 72% and 88% of the total endpoint with the GripX coating (route 1a) and without it (route 1b), respectively. Hence, from an environmental perspective, the liberation of the MFC should be the focus of efforts to improve the production process. Looking closely at the liberation process (see Figure 3) revealed that the enzymatic treatment step was responsible for the highest share of environmental impact. This was mainly due to the energy needed to heat and stir the mixture at 40 °C for 24 h. Although heating to this temperature does not seem to be very energy intensive, it becomes apparent when considering the high water content of carrots (~87%).[23] To obtain 150 g of liberated MFC, about 15 kg of carrot waste suspended in 15 kg of water (30 kg of suspension) must be heated for 24 h. The lower efficiency, due to the heat loss in the laboratory process, also added to the impact. Evaluating the midpoint results for wet spinning (Figure 4) showed clearly that the use of acetone (in the solvent exchange and drying step after the spinning) had a high potential for photochemical oxidant formation. This results mainly from the acetone evaporating and being emitted into the air during the drying step. The spinning process results in a further significant use of water resources. GripX, on the other hand, had a higher relative contribution to the terrestrial ecotoxicity potential deriving from the hazardous solvent waste that is produced during its production; this goes to a hazardous waste incineration plant.

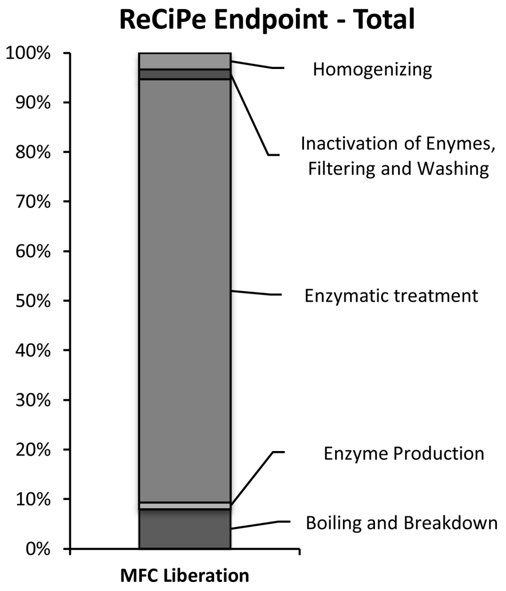

Figure 3. *ReCiPe* end point indicator for MFC liberation divided into process steps.

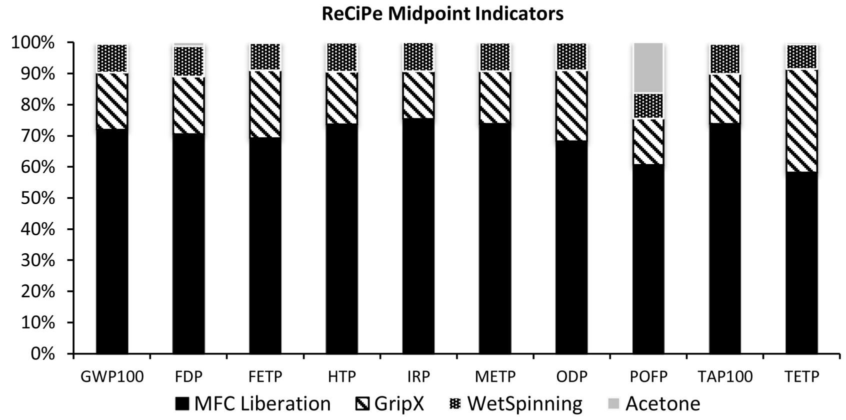

Figure 4. *ReCiPe* midpoint indicators for route 1a, showing: global warming potential (GWP100); fossil fuel depletion potential (FDP); freshwater ecotoxicity potential (FETP); human toxicity potential (HTP); ionizing radiation potential (IRP); marine ecotoxicity potential (METP); ozone depletion potential (ODP); photochemical oxidant formation potential (POFP); terrestrial acidification potential (TAP100); terrestrial ecotoxicity potential (TETP).

Comparison with Other Nanocellulose Studies. The two published LCA studies of laboratory-scale nanocellulose production that we compared to our technology used different starting materials and extraction processes. Figueirêdo et al.[15] examined the production of nanocellulose from white cotton and unripe coconuts via a chemical acid hydrolysis using sulfuric acid. The process starting from unripe coconuts needed pretreatment because of their high lignin content. Table 3 compares various *ReCiPe* midpoint indicators for the extraction of 1 g of MFC using our technology (i.e., out of carrot waste) with the results from this Brazilian study.

Table 3. Selected ReCiPe Midpoint Indicators per 1 g Extracted MFC of the Process Developed in This Study Compared to Figueirêdo et al. (2012)[15] Using the Adapted Brazilian Electricity Mix

process	electricity input [kWh]	electricity mix (voltage)	climate change [kg CO_2 eq]	human toxicity [kg 1,4-DB eq]
cotton	0.4	Brazil (low)	0.122171	0.034797
unripe coconuts	3.64	Brazil (low)	1.086412	0.291122
carrot waste	0.20	Europe (med)	0.1068887	0.0687255
(with carrot prod.)			(0.1416519)	(0.0802657)
carrot waste	0.20	Brazil (low)	0.0607549	0.0175412
(with carrot prod.)			(0.0955181)	(0.0290813)

To compare technologies and not the locations of production, our technology's indicators were recalculated using the Brazilian electricity mix. Based on the results for all the midpoint indicators examined, our technology performed substantially better than the unripe coconut extraction process; the cotton process did better, but results still favored our technology when the Brazilian electricity mix was used. When the production of the carrots themselves was accounted for and no longer regarded as a free input, the results came very close to the cotton-using case. The global warming potential of the coconut and cotton processes were 17.8 and 2.0 times greater than for our technology, respectively. This was in line with the electricity needed for the production of 1 g of nanocellulose (18.2 and 2 times greater, respectively). Thus, this difference in the climate change midpoint was mainly caused by the differences in direct electricity consumption of these processes. A similar picture was found for human toxicity potential, which differed by factors of 16.6 and 2.0, respectively.

Li et al.[16] assessed different production routes for nanocellulose from wood pulp, where a chemical process is followed by mechanical treatment. The chemical step is either a TEMPO-oxidation (TO) or a chloroacetic acid etherification (CE), whereas the mechanical process involves homogenization (HO) or sonication (SO). In the present study, we compared our technology to these processes by recalculating our process using the US electricity mix. However, the database used to compare US electricity was not the same one as Li et al. used (i.e., the USLCI database from 2000). To circumvent errors from those different background data, we calculated the impact per kWh of electricity for each impact category in the results provided by Li et al. This calculation was possible because the sole input for sonication and homogenization is electricity. Our process used the calculated impact per kWh to give results simulating the same electricity mix. Table 4 shows the results from this comparison.

The direct electricity input in the mechanical homogenization process is about half the amount used in our carrot waste process. Applying the sonication process, on the other hand, uses far more electricity than both the above processes. The total CED of our enzymatic extraction process is nevertheless lower than all the wood pulp based production processes, i.e., the HO and SO processes. We must look beyond the electricity use of the processes themselves to find the reason for this. A high portion of the CED is generated by the chemical inputs used in the production processes; these become apparent when the impacts without the contribution of electricity are evaluated, the wood pulp production process used for the input is contributing to that, too. In the carrot waste process, electricity accounts for at least 95% of the CED as the whole reaction takes place in water and, therefore, almost no chemicals are used. The wood pulp-based processes, however, still have significantly high remaining impact values without electricity. The main contributors are the ethanol and isopropyl alcohol that are consumed in large quantities. A similar pattern is observed for the global warming potential, although the share of the electricity is higher for the wood pulp-based processes as

Table 4. Comparing our Process to the Li et al. (2013)[16] Process for Selected Impact Categories per 10 g of Liberated MFC, with Adapted US Electricity Mix

process	electricity input [kWh]	electricity mix (voltage)	CED total [MJ eq]	CED nonrenewable [MJ eq]	CED renewable [MJ eq]	IPCC7 GWP 100a [kg CO_2 eq]	Eco-indicator 99 H/H [points]
CEHO[a]	1.150	US (low)	64.9	48.8	16.1	3.6	0.35
(without electricity contr.)[b]	(0)		(52.4)	(36.3)	(16.1)	(2.7)	(0.30)
CESO[a]	11.344	US (low)	176.1	160.0	16.1	11.6	0.78
(without electricity contr.)[b]	(0)		(52.4)	(36.3)	(16.1)	(2.7)	(0.30)
TOHO[a]	1.095	US (low)	34.7	19.5	15.2	1.9	0.16
(without electricity contr.)[b]	(0)		(22.8)	(7.6)	(15.2)	(1.0)	(0.12)
TOSO[a]	11.289	US (low)	145.9	130.6	15.2	9.8	0.6
(without electricity contr.)[b]	(0)		(22.8)	(7.6)	(15.2)	(1.0)	(0.12)
carrot waste	2.000	Europe (med)	22.8	21.4	1.4	1.1	0.052
[with carrot prod.]			[29.8]	[26.0]	[3.8]	[1.4]	[0.077]
carrot waste	2.000	US (*ecoinvent*)	25.2	24.3	0.9	1.5	0.064
(without electricity contr.)	(0)		(0.2)	(0.2)	(0.02)	(0.02)	(0.003)
[with carrot prod.]	[2.000]		[32.2]	[28.9]	[3.2]	[1.9]	[0.088]
carrot waste	2.000	US (calculated)[b]	22.0	22.0	0.0	1.6	0.087

[a]TO, TEMPO-oxidation; CE, chloroacetic acid etherification; HO, homogenization; SO, sonication. [b]Calculated based on results and data from the Supporting Information..

the electricity mix used produces large amounts of greenhouse gases. Here, the impact of the TOHO process (1.9 kg CO_2 equiv) comes very close to our process (1.5 or 1.6 kg CO_2 equiv). However, the chemicals have a high impact on the *Eco-indicator 99* results: the TOHO process does not compare as well to our process as it does in the previous category, despite the fact that it uses almost half the electricity.

■ DISCUSSION AND OUTLOOK

In the new technological process presented in this study, whichever production route is followed to the final spun yarn, electricity use is the main contributor to the LCIA. This is because mostly water is used for the processing and only relatively small quantities of (hazardous) chemicals are needed. Furthermore, the starting material (i.e., carrot waste) can be modeled as a free input with no environmental burdens resulting from its production. When electricity use is the main contributor to LCIA, the results strongly depend on the specific electricity mix (composition of energy production sources) and these vary significantly with the geographical location. Since a large portion of the electricity use in our process is needed for heating purposes, scaling it up to an industrial scale would make the LCA results less electricity dependent as industrial-sized chemical heating processes mainly use natural gas or other fossil fuels.

Second, a detailed analysis of the results indicated that, with the current equipment, the wet-spinning process route is clearly the preferred option for spinning nanocellulose yarn. To a certain extent, this result was caused by the much lower scale of production used for electrospinning; this differed by a factor of over 60, and smaller-scale production is generally associated with lower energy efficiency and yields. However, if electricity use and yield losses were lowered by a significant amount, at a larger scale of production and by developing an improved process, then electrospinning might become a competitive alternative from an environmental perspective. The present study's results could therefore be used to optimize this production step.

To improve the production of wet-spinning route 1 (a or b), research and development should concentrate on MFC liberation, especially the enzymatic treatment, as the analysis showed that this was the main contributor to the environmental impact. Of course, optimization efforts should not completely exclude other stages. Decreasing energy consumption during the enzymatic treatment step could be achieved by reducing the amount of water added to the suspension, improving heating efficiency through better insulation and/or heat recovery and reducing the length of the reaction time and/or its temperature. All these measures could potentially result in a significant reduction of this new technology's overall environmental impact. Minimizing heat loss would seem to be the simplest measure, especially if the technology went to industrial-scale production, given that the process was performed at a laboratory scale where insulation and heat exchange were not optimized. Another measure to reduce the environmental impact of the wet-spinning process, especially with regard to its potential for photochemical oxidant formation, would be to reduce or even eliminate the use of acetone for the solvent exchange. If this proved impossible, preventing the vaporized acetone from being emitted into the air would also be beneficial. To improve the production of GripX, solvent waste could be reduced by using a proper recycling procedure, such as distillation and/or reducing the amount for product required for the reaction.

Were a commercial application of this process to use carrot pomace as the starting material, the relative necessary processing quantities would be lowered considerably for the amount of fibers obtained because pomace has a much higher

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cellulose content (~24 wt % compared to 1−1.5 wt %). The resulting higher mass yield, combined with the lower processing quantities, would presumably lower the environmental impact. Furthermore, the polysaccharide byproducts from the enzymatic treatment step were placed outside the system boundaries. In a large-scale application, these could be used as inputs for other processes, which would make a system expansion or allocation necessary. This would further lower the environmental impact of the nanocellulose produced with this technology.

The present study showed that the water-based enzymatic process had environmental advantages over other nanocellulose extraction technologies. The LCA revealed that the lower electricity input (other than for the CEHO and TOHO cases), the conservative use of chemicals as solvents and/or reactants, the larger production scale and, to a minor degree, the impact-free starting material input were all reasons for the favorable results. On the basis of this study, we concluded that the newly developed MFC extraction technology seemed to be a promising and sustainable alternative production route for nanocellulose fibers. However, as a part of the overall technology development process, this study only evaluated the environmental impact of the laboratory-scale process and the results gave no indication about the quality of the obtained material. The results of such a laboratory-scale comparison are meant to serve as a benchmark and give researchers a qualitative assessment of the technology compared to others. The absolute values of laboratory-scale LCAs should therefore be treated with caution.

We used LCA at an initial laboratory stage in order to obtain a better understanding of the production process as early on as possible in the overall technology development process. It gives an indication about which steps should be treated as priorities in order to optimize the technology from an environmental perspective. Hence, researchers will be able to implement the results of this study to adapt the process immediately.

This study shares in some of the limitations of a laboratory-scale LCA, as its results cannot be linearly translated to industrial-scale production: the process steps may differ substantially after scaling-up. A (theoretical) scale-up process, to an industrial MFC production plant, could be the next step; this should also bring more information about the scalability of the various process steps and the resulting implications for environmental performance at larger scales. An industrial-scale LCA will allow comparisons with other competing materials and other life cycle stages (use or end-of-life) can be added. This requires that the application field of the material is included using appropriate functional units.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data about the LCA calculations on input materials. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00209.

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Notes

The authors declare no competing financial interest.

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