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Life Cycle Assessment of Cellulose Nanofibrils Production by Mechanical Treatment and Two Different Pretreatment Processes

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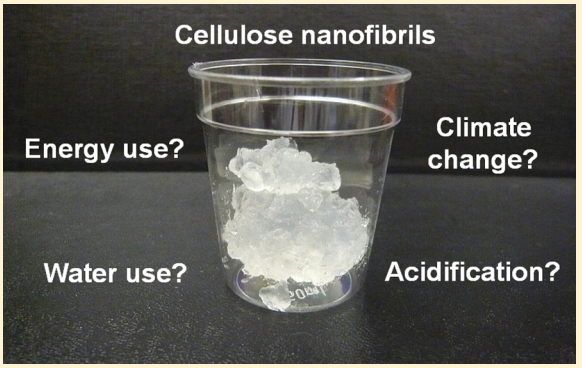
Supporting Information

ABSTRACT: Nanocellulose is a bionanomaterial with many promising applications, but high energy use in production has been described as a potential obstacle for future use. In fact, life cycle assessment studies have indicated high life cycle energy use for nanocellulose. In this study, we assess the cradle-to-gate environmental impacts of three production routes for a particular type of nanocellulose called cellulose nanofibrils (CNF) made from wood pulp. The three production routes are (1) the enzymatic production route, which includes an enzymatic pretreatment, (2) the carboxymethylation route, which includes a carboxymethylation pretreatment, and (3) one route without pretreatment, here called the no pretreatment route. The results show that CNF produced via the carboxymethylation route clearly has the highest environmental impacts due to large use of solvents made from crude oil. The enzymatic and no pretreatment routes both have lower environmental impacts, of similar magnitude. A sensitivity analysis showed that the no pretreatment route was sensitive to the electricity mix, and the carboxymethylation route to solvent recovery. When comparing the results to those of other carbon nanomaterials, it was shown that in particular CNF produced via the enzymatic and no pretreatment routes had comparatively low environmental impacts.



1. INTRODUCTION

Nanomaterials are increasingly being produced and used in society.[1] A concern over this development is the life cycle environmental impacts of nanomaterials and nanoproducts.[2,3] In response to this, a number of life cycle assessment (LCA) studies have been conducted to assess cradle-to-gate environmental impacts related to nanomaterials. These studies include assessments of fullerenes,[4,5] carbon nanotubes,[5−8] carbon nanofibers,[9] graphene,[10] molybdenum sulfide,[11] and titanium dioxide nanoparticles.[12,13] These cradle-to-gate studies are typically conducted in order to improve the environmental performance of the nanomaterial production, thereby also reducing the environmental impact of any products in which the nanomaterial may be subsequently used. A review of LCA studies on nanomaterials indicated that many nanomaterials are more energy-intensive than comparable, traditional materials, such as aluminum, steel, and polypropylene.[14] One reason for this higher environmental impact is that production processes are comparatively advanced and include more precise control of the resulting properties of the material. Another is that most nanomaterials are in an early stage of technological development, at which lab-scale processes with higher energy and material use are employed. There also exist a number of studies of products that contain nanomaterials as one among several constituents—some that are cradle-to-gate studies and some that are cradle-to-grave.[15] Such studies include nanomaterials such as nanosilver[16−18] and carbon nanotubes.[19,20] Challenges in conducting LCA studies of nanomaterials include data unavailability, particularly related to the use and end-of-life phases, and the lack of characterization factors for assessing impacts of emissions of nanoparticles.[15] Consequently, there are so far only a few studies assessing environmental impacts of emissions of nanoparticles.[8]

This study concerns nanocellulose, which was first mentioned in the scientific literature by Turbak et al.[21] Nanocellulose is a bionanomaterial with many promising properties, including high strength and transparency. It has received increasing attention in the scientific community according to bibliometric studies[22−24] and can be used in numerous products, such as nanocomposites for improved construction materials and transparent films for food packaging.[25,26] Rebouillat and Pla estimated global production capacity of nanocellulose to be on the order of 600 metric

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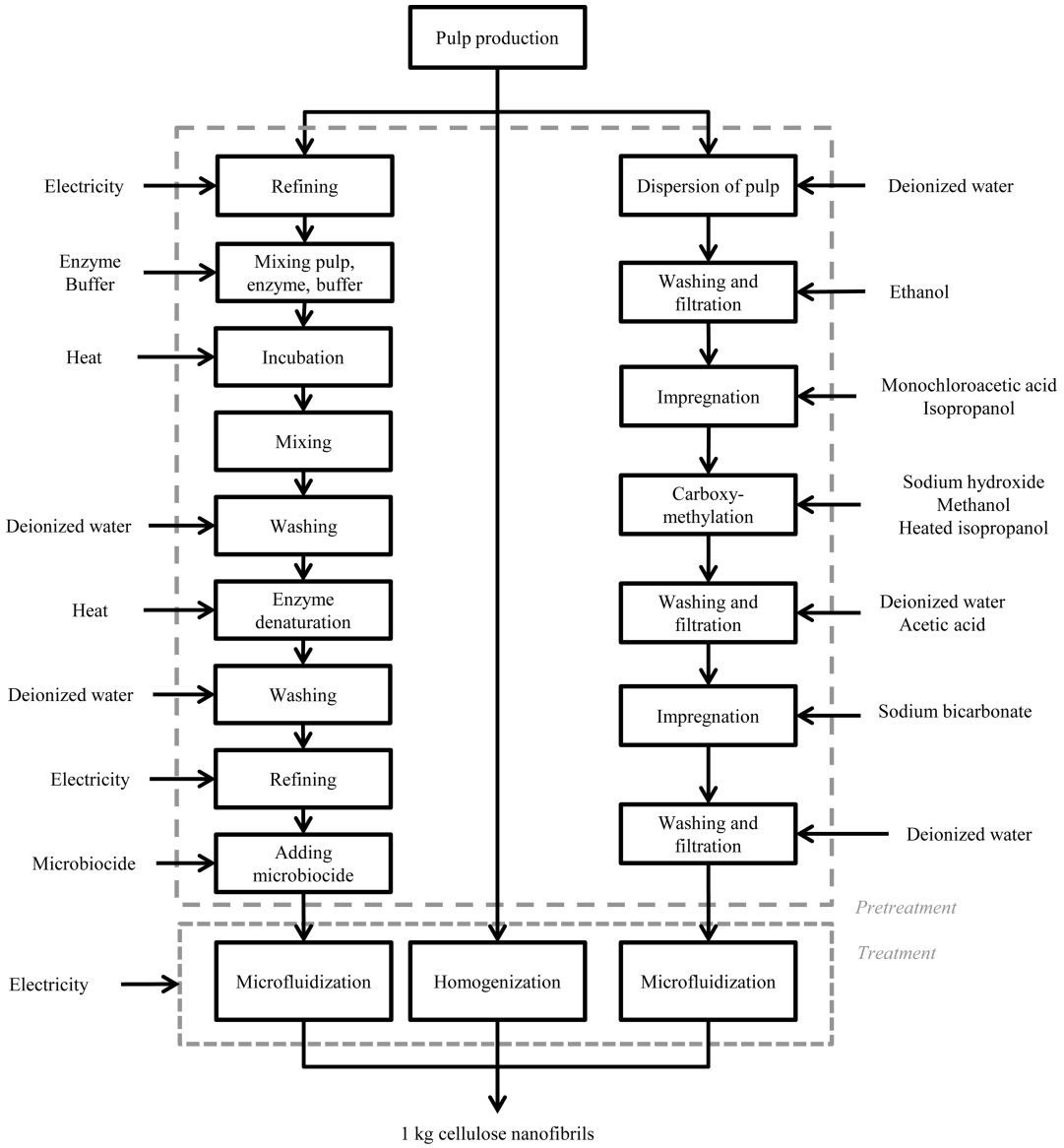

Figure 1. Flowchart of the studied system, showing the three studied production routes: (1) the enzymatic route (to the left), (2) the carboxymethylation route (to the right), and (3) the no pretreatment route (in the middle).

tonnes/year in 2013,[27] and the future global market potential has been estimated to be 35 million metric tonnes/year.[28,29]

Nanocellulose can be categorized into three types: nanofibrillated cellulose (sometimes called microfibrillated cellulose), nanocrystalline cellulose (sometimes called nanowhiskers), and bacterial cellulose.[30] According to the Technological Association of the Pulp and Paper Industry (TAPPI), the first two of these are termed cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC), respectively.[31,32] CNF consists of both crystalline and amorphous regions of 5−30 nm width and a height typically 50 times longer. CNC consists of a purely crystalline structure of 3−10 nm width, with a height more than 5 times longer. Bacterial nanocellulose (BNC) consists of networks of nanosized fibers that are synthesized by bacteria, with diameters of 20−100 nm.

In general, CNF production routes can be described in terms of (1) pretreatment processes, in which the cellulose is pretreated before the final treatment, and (2) treatment processes, in which the cellulose is turned into CNF.[27] Pretreatment processes are conducted in order to facilitate subsequent disintegration into CNF—thus, pretreated cellulose is already partly disintegrated. Concerns have been raised regarding high energy use from nanocellulose production, in particular from the treatment process, which has been described as the "Achilles' heel" of CNF.[18,23] There are to date two LCA studies on nanocellulose published in the scientific literature. Li et al. assessed the production of wood-based CNF from four different production routes, which included two different pretreatment processes and two different treatment processes.[33] The two pretreatment processes were 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation and chloroacetic acid etherification, and the two treatment processes were sonication and homogenization. In the study by de Figueirêdo et al., production of CNC from cotton and coconut fibers by acid hydrolysis was assessed.[34] The results from these two studies are further discussed in the Results and Discussion section, but in general they indicate high life cycle energy use.

In the study reported in this paper, life cycle environmental impacts of CNF produced via three production routes were assessed: (1) the enzymatic route, with an enzymatic

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pretreatment and a microfluidization treatment, (2) the carboxymethylation route, with a carboxymethylation pretreatment and a microfluidization treatment, and (3) the no pretreatment route, which has only a homogenization treatment. To the best of our knowledge, the life cycle impacts of these routes have not been assessed before, although the carboxymethylation pretreatment is similar to the chloroacetic acid pretreatment assessed by Li et al.[33] These three routes are currently studied by the research institute Innventia in Sweden,[24] which has a demonstration plant for CNF production.[27] The third route, with no pretreatment, is the route most commonly used in experimental studies[22] and was the only route before the invention of pretreatment processes in the 2000s. Together with the TEMPO oxidation assessed by Li et al.,[33] these three routes are the most referred to in scientific documents.[22]

The first aim of this study is to assess the life cycle environmental impacts of CNF production for the three different production routes, with a thorough sensitivity analysis. Based on this, the second aim is to point to reduction opportunities for the life cycle impacts in future, large-scale production. The third aim is to compare the results to those of previous LCA studies of carbon nanomaterials with similar potential uses, in order to investigate whether CNF has comparatively high environmental impacts. Since this is a cradle-to-gate study, the intended audience of the study is primarily companies and researchers producing, purchasing, and studying CNF. However, considering the general concern for environmental impacts of new nanomaterials, the study should also be of interest for a more general audience, including policy makers.

The most commonly discussed environmental issues for nanomaterials today are direct toxic and ecotoxic effects resulting from exposure to the nanomaterial itself.[35−37] Vartiainen et al. found low toxicity of CNF to both mouse and human cells, and to *Daphnia magna*.[38] Similarly, Alexandrescu et al. found no toxicity of CNF to human cells.[39] For CNC, Yanamala et al. wrote that some studies had reported little or no toxicity to human cells and aquatic species but also reported that some studies had shown pulmonary effects.[40] Their own study confirmed pulmonary effects, which for some variants of CNC exceeded those of asbestos fibers. However, such direct impacts of CNF were not considered in the present study, since no emissions of CNF from the production routes studied have been confirmed or otherwise indicated.

2. METHOD AND MATERIALS

The method used in this study is LCA as described by, for example, Baumann and Tillman,[41] Hellweg and Milà i Canals,[42] and the ISO[43] standard. This study is an attributional and prospective LCA of an emerging product, similar in scope to the studies by Walser et al.[17] and Arvidsson et al.[10] The goal of the study is to assess cradle-to-gate life cycle impacts of CNF production. This means that the study includes the life cycle from raw material extraction to, and including, production of CNF. A cradle-to-gate perspective is particularly relevant for materials that have many subsequent applications, of which some have not yet been developed. Cradle-to-gate results can then be used in subsequent cradle-to-grave studies of products in which the studied material, in this case CNF, is one constituent. The functional unit of the study is 1 kg, which is a common functional unit for cradle-to-gate assessments of nanomaterials, and enables comparison of impacts across nanomaterials.[14]

Since CNF is an emerging and still immature product, the technical system is partly under development. The challenges that arise when conducting assessments of emerging products include data unavailability, scale-up effects, choosing a relevant functional unit, and comparability to existing products.[44] A prospective LCA, in which the environmental impacts of an emerging or immature product are to be assessed, must thus address the uncertainties that come with these challenges.[45,46] In order to investigate the inherent uncertainty in the technical system brought on by its emerging nature, a thorough sensitivity analysis was made, and the influence of scale-up and changes in background systems are discussed in this paper.

A flowchart describing the studied production system is shown in Figure 1. This system follows the experimental studies in which these processes were described. In general, there have been three main sources of data. The first is a personal communication with Eva Ålander, senior research associate at the research institute Innventia, who provided information about relevant production routes to investigate.[47] The second is the publications by Ankerfors,[24] Pääkkö et al.,[48] and Wågberg et al.,[49] which contain original data on CNF production. The third is the Ecoinvent database (version 2.2),[50] from which inventory data for production of mature, established products has been obtained. A list of input materials and energy for these processes can be found in Table 1, and detailed information about included background processes and data sources is provided in the Supporting Information (SI). The yields of all three routes are effectively 1, meaning that very little raw material is lost during the pretreatment and treatment processes.

Table 1. List of Inputs Per Functional Unit for the Baseline Scenarios of the Two Pretreatment Processes and the Treatment Process (Obtained from References 24, 48, and 49)

input	amount
enzymatic pretreatment	
pulp	1.0 kg
enzyme	0.00017 kg
phosphate buffer (11 KH_2PO_4: 9 Na_2HPO_4)	0.042 kg
deionized water	130 kg
microbiocide	0.010 kg
heat	9.6 MJ
electricity for refinement	0.44 MJ
carboxymethylation pretreatment	
pulp	1.0 kg
ethanol	7.2 kg
monochloroacetic acid	0.090 kg
isopropanol	18 kg
sodium hydroxide	0.15 kg
methanol	3.6 kg
acetic acid	0.10 kg
sodium bicarbonate	0.76 kg
deionized water	480 kg
heat	2.3 MJ
treatment	
electricity with pretreatment (microfluidization)	8.0 MJ
electricity without pretreatment (homogenization)	72 MJ

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2.1. Impact Categories. In this study, four impact categories were selected: energy use, climate change, acidification, and water use. Energy use is an important resource use impact category, which has been shown to correlate well with several types of environmental impacts.[51,52] Energy use is also of particular importance since CNF production without pretreatment has been reported to have high energy use in experimental studies.[24] Climate change is an important environmental aspect, also for biobased systems.[53] Acidification is an emission-based impact category and does not always correlate with climate change for biobased systems and thus gives a different perspective on environmental impact. Water use is a resource use impact category that gives a different perspective than energy use and is an important aspect of biobased products.[54] These together give a broad perspective on the environmental and resource impacts of CNF.

It is important to be clear and transparent regarding energy use indicators in LCA, in particular for biobased systems.[55] In this study, the energy use is calculated as cumulative energy demand (CED), measured in MJ. The main principle of CED is to include all energy withdrawn from nature.[56] Thus, all energy use is recalculated to their primary energy sources, both renewable and nonrenewable energy are included, and the feedstock energy for input materials is also included.

The other included impact categories are operationalized as the global warming potential (GWP), terrestrial acidification (TA), and water depletion (WD) midpoint indicators from the ReCiPe impact assessment method.[57] A hierarchist scenario is selected, in which the most common time frames in contemporary policy are assumed (e.g., 100 years for GWP). The indicators are measured in kilograms of CO_2 equivalents (eq), kilograms of SO_2 eq, and cubic meters, respectively.

2.2. Production of Pulp. In general, CNF can be produced from any cellulosic substrate by breaking some of the bonds that hold cellulose fibers together. Wood pulp is an attractive starting material since it consists of cellulose fibers which have already been partly broken down and are therefore already on the route of being transformed into CNF.[58] Wood pulping is also a common process, generating large volumes of pulp in many parts of the world. Two main categories of pulp are sulphite and sulfate pulp (of which the latter is also referred to as kraft pulp). The main difference between these two types is which chemicals that are used to dissolve the lignin during the pulping process. In response to concerns about dioxins from chlorine bleaching in pulping, pulp can be elementary chlorine free (ECF), totally chlorine free (TCF), or even unbleached.[59] In this study, four different types of pulp, for which data are available in the Ecoinvent database, were considered: ECF sulfate, TCF sulfate, unbleached sulfate, and chlorine bleached sulphite pulp. These four pulp types can all be used for CNF production.[47] The data include wood production, transports to the pulp mill, chemical pulping and bleaching, drying, energy production on-site (from black or brown liquor), recovery cycles of chemicals, and internal wastewater treatment.[50] The origin of the data is mainly Scandinavian producers and conditions.

Unbleached sulfate pulp generally had the lowest environmental impact and was selected for the baseline scenario. Chlorine bleached sulphite pulp had the highest environmental impacts, and the influence of switching to this pulp was therefore tested in the sensitivity analysis.

2.3. Enzymatic Pretreatment. In the enzymatic pretreatment (Figure 1), the pulp cellulose is disintegrated due to the acting of enzymes upon the cellulose in the pulp. Data for this process were obtained from experiments reported by Pääkö et al.[48] (Table 1). Before and after the application of enzymes, refining is conducted in order to avoid clogging in the treatment process. The type of enzyme used is endoglucanase, a form of cellulase, which can break glucosidic linkages in cellulose. This facilitates the subsequent treatment process. The enzyme product used was "Novozym 476, Novozym A/S." Based on personal communication with industry representatives from the company Novozymes in Denmark, Liptow et al. reported aggregated environmental impacts of their cellulase enzyme products.[60] Because of a lack of more specific data on enzyme production, these data have been assumed to correspond to the enzyme product used in the enzymatic pretreatment.

In order for the enzymes to work effectively, a phosphate buffer must be applied. In the original experiments, the buffer consisted of a combination of monopotassium and disodium phosphate (11 KH_2PO_4: 9 Na_2HPO_4). Considering the availability of inventory data in the Ecoinvent database, however, this buffer was substituted for the similar substance trisodium phosphate buffer (Na_3PO_4) in this study. The replacement of 11 KH_2PO_4: 9 Na_2HPO_4 by Na_3PO_4 was done based on stoichiometry, see the SI. A microbiocide (5-chloro-2-methyl-4-isothiazolin-3-one) is added in order to prevent bacterial growth. However, due to a lack of inventory data and low mass input (~0.01 kg/kg CNF), this input material was omitted. (Note that the biocide should have high ecotoxicity, so studies including that impact category should consider including this input material despite low mass input.) Deionized water is required in the washing steps of the process. Inventory data for deionized water were obtained from the Ecoinvent database.

Two temperature alterations are reported. These are the increase from room temperature (21 °C) to 50 °C during the incubation time when the enzymes are active and later in the process denaturation of the enzymes by increasing the temperature from room temperature to 80 °C. The energy required for this was calculated using the following equation:

$$E = c \times m \times \Delta T \quad (1)$$

where E is the required energy for the temperature change, c is the heat capacity of the solvent (in this case water), m is the mass of the solvent, and ΔT is the temperature change.

2.4. Carboxymethylation Pretreatment. In the carboxymethylation pretreatment (Figure 1), negatively charged carboxymethyl groups are introduced to the cellulose in the pulp. This addition of negative charges creates an electrostatic repulsion that facilitates separation into CNF in the treatment process. This process is described by Wågberg et al.,[49] and input data for this process can be found in Table 1. Note that it is the monochloroacetic acid that provides the carboxymethyl groups to the cellulose in the pulp by means of the following reaction:

$$ROH + CH_2ClCOOH \rightarrow ROCH_2COOH + HCl \quad (R1)$$

where R represents the rest of the cellulose molecule. The ethanol, isopropanol, and methanol are used as solvents. The sodium hydroxide neutralizes hydrochloric acid formed in the carboxymethylation reaction, and the sodium bicarbonate adds sodium instead of hydrogen ions to the carboxymethylated CNF. The acetic acid and deionized water are used for washing.

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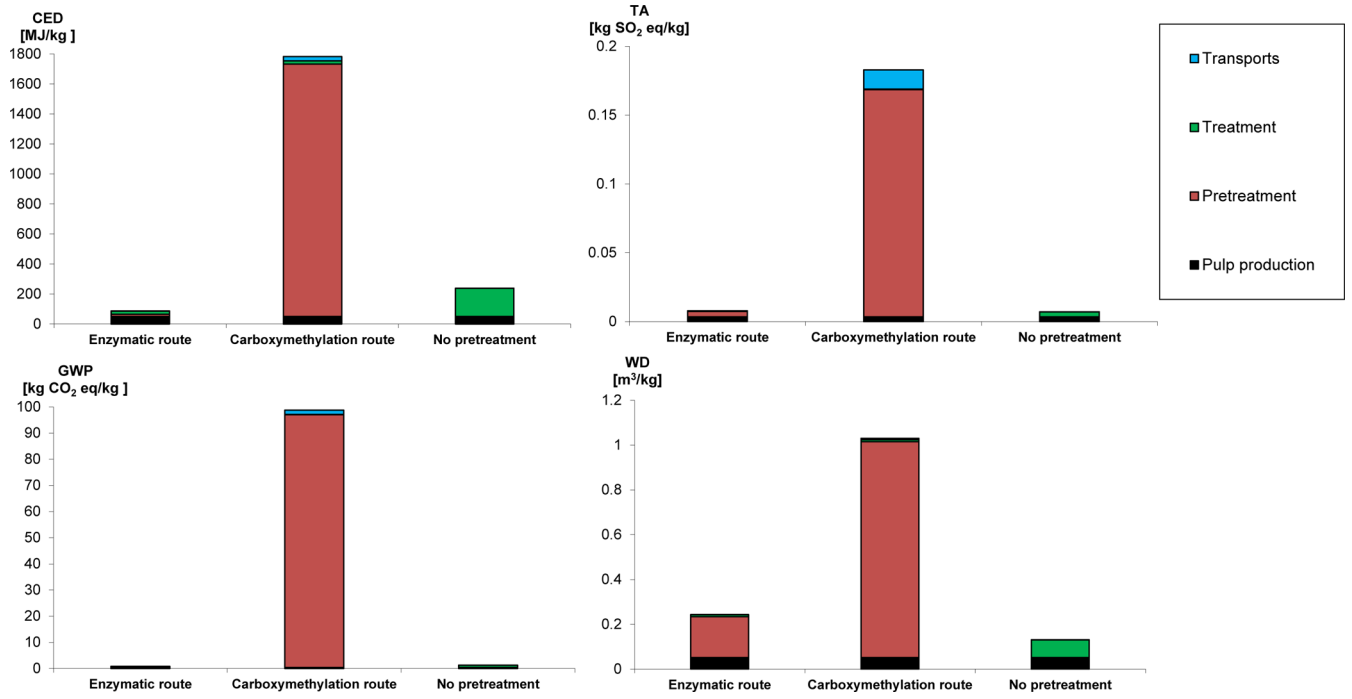

Figure 2. Life cycle assessment results for the baseline scenarios of the three studied production routes for cellulose nanofibrils (CNF). CED is cumulative energy demand. GWP is global warming potential. TA is terrestrial acidification, and WD is water depletion.

Inventory data for all input materials were obtained from the Ecoinvent database. For sodium bicarbonate ($NaHCO_3$), no inventory data existed, but instead data were taken for production of sodium carbonate (Na_2CO_3). The rationale for this is that these materials are often produced in a similar way by the Solvay process, and the function of this input is to provide sodium ions, which both substances possess. The equivalent amount of sodium carbonate required was calculated on a stoichiometric basis, see the SI.

Whereas the other input materials have typical production routes, ethanol is often produced either from ethylene from crude oil or from starch-containing feedstock such as corn. Ethanol from crude oil was assumed in the baseline scenario since it is more frequently used as an industrial chemical and due to its lower environmental impacts, and corn-based ethanol was tested as an alternative in the sensitivity analysis. Inventory data were obtained from the Ecoinvent database in both cases.

During the carboxymethylation pretreatment, some isopropanol is heated from room temperature to its boiling temperature of 83 °C. The energy required to do so was calculated using eq 1.

No handling of the remaining solvents (methanol, ethanol, and isopropanol) is reported.[49] We considered the used solvents as liquid organic waste, which was sent for incineration. Inventory data were obtained from the Ecoinvent database for waste solvent mixture incineration with added heat from oil and natural gas boilers. The required heat was adjusted for the higher heat value of the alcohols compared to the waste solvents in Ecoinvent. Possibilities for recovery of heat and material from solvents are discussed in the sensitivity analysis.

2.5. Treatment. In the treatment phase, CNF is produced from the (potentially pretreated) pulp. Ankerfors estimated the electricity use from treatment through microfluidization after enzymatic and carboxymethylation pretreatment to 8.0−8.4 MJ/kg.[24] This range was applied in the sensitivity analysis for both the enzymatic route and the carboxymethylation route, with 8.0 MJ/kg as the baseline scenario.

For the no pretreatment route, 97 MJ/kg CNF is reported by Ankerfors for the homogenization treatment.[24] However, there are also reports of homogenization electricity use of 72−108 MJ/kg.[61] This wider range was tested in the sensitivity analysis, with 72 MJ/kg as the baseline scenario representing efficient future production.

The output CNF product from the treatment is considered to be in the form of 2 weight-% CNF in water, for all three routes, which is a common output from CNF preparation.[26] The CNF products from the three routes are similar in terms of fiber size (∼5−30 nm width, ∼1−2 μm length).[24] However, CNF from the carboxymethylation route has carboxymethyl groups attached to the cellulose molecules. This difference has no major influence on the subsequent use of the CNF as a reinforcement in composites. For use in transparent films, however, it has been shown that CNF produced by the carboxymethylation pretreatment has lower turbidity (i.e., higher transparency),[24] so for this purpose, the fibers are not functionally equivalent. Lower turbidity of CNF from the enzymatic route can be obtained by additional microfluidization, which would bring a higher energy requirement. This should be taken into account in future LCA studies of CNF used in transparent films.

2.6. Transport. Considering the emerging nature of CNF production, exact future transport distances and modes of transport cannot be known. Therefore, a set of reasonable transport scenarios were developed, see the SI for details. Pulp production in both Sweden and Russia, and enzyme production in Denmark, were considered in terms of transportation distances. For other input materials, both transports from Germany and China were considered. In general, the calculation of the impacts of the transports (I) was conducted by multiplying the transport distance x, the mass transported m, and the impact per kilogram and kilometer ($I_{kg\cdot km}$, which varies

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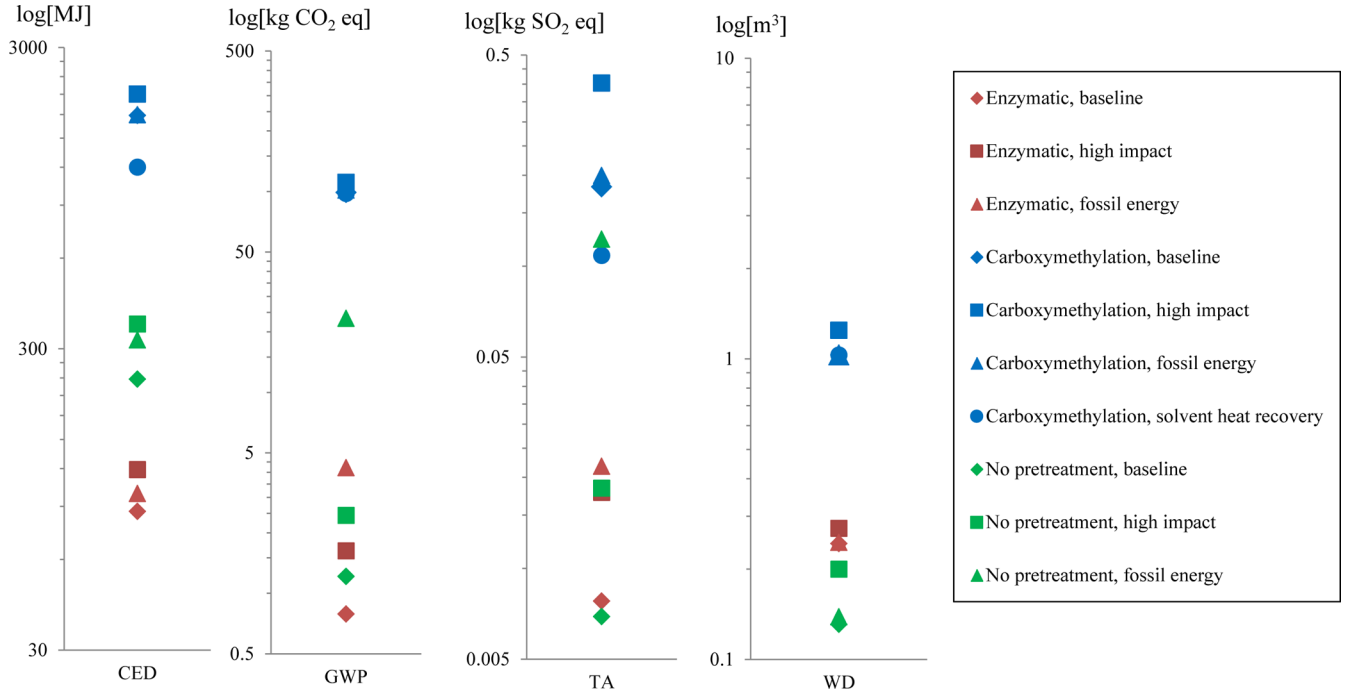

Figure 3. Results from the sensitivity analysis. The high impact scenario employs pulp production, treatment energy use, transports, and ethanol production with higher environmental impact. The fossil energy scenario employs fossil electricity and heat. In the solvent heat recovery scenario, heat from fossil waste solvents is recovered in the carboxymethylation route. Note that the scales are logarithmic. CED is cumulative energy demand. GWP is global warming potential. TA is terrestrial acidification, and WD is water depletion.

for different modes of transport) for each transport distance i included in a transport scenario S. The impact of a transport scenario is thus calculated as

$$I_S = \sum_i x_i \times m_i \times I_{\text{kg·km}},\ i \in S \tag{2}$$

From the scenarios, a baseline scenario with the lowest environmental impact was identified for all three routes, and the influence of switching to the worst case scenarios with high environmental impact was tested in the sensitivity analysis.

2.7. Electricity Mix, Heat Source, and Heat Losses. The electricity mix used in the three routes was assumed to be Swedish electricity mix (approximately half hydro and half nuclear), considering the location of Innventia in Sweden and the high likelihood of CNF production being performed at Swedish pulp mills in the future. This mix was obtained from the Ecoinvent database, and the influence of changes in the electricity mix was tested in the sensitivity analysis.

The heat source assumed was biomass, since that is how much heat in Sweden is generated. It also reflects a potential future integration of CNF production with biorefineries, as is being researched for CNC.[62] Since no data on heat production from biomass are available in the Ecoinvent database, data for a biomass boiler were obtained from the United States' life cycle inventory database, specifically the data set "Combustion, dry wood residue, AP-42."[63] The influence of changing heat source is tested in the sensitivity analysis.

Heat losses during the enzymatic and carboxymethylation pretreatments were calculated using the mechanical insulation design guide provided by the United States' National Institute of Building Science,[64] see the SI. For all cases, heat losses were low, <0.002 MJ of heat per kg of CNF. Considering this negligible contribution to the overall CED, heat losses were excluded from the calculations.

3. RESULTS AND DISCUSSION

3.1. Baseline Scenario Results. Figure 2 shows the cradle-to-gate life cycle impacts of CNF for the assessed impact categories. For all four impact categories, it is clear that the carboxymethylation route has the highest impact. The result for CED is particularly interesting, since the main concern over CNF energy use has been high energy use in the treatment process.[24] Pretreatment processes have been developed in order to lower the energy use of CNF. However, from a life cycle perspective, the carboxymethylation route has a higher CED than the no pretreatment route, and it is the pretreatment process that is particularly energy-demanding. More specifically, the high impact comes mainly from the almost 30 kg/kg CNF of the input chemicals ethanol, isopropanol, and methanol. Reduction of this high chemical use is thus the most obvious way to reduce the CED of this route, for example through solvent recovery if technically feasible. This is discussed further in the sensitivity analysis.

The environmental impacts of the enzymatic route and the no pretreatment route are of similar magnitude for the four impact categories. For the enzymatic route, pulp production is the main contributor to CED and GWP, whereas the enzymatic treatment is the main contributor to TA (due to phosphate buffer production) and WD (due to water use for washing). Reducing the direct water use for washing would thus be a way to reduce the WD of the enzymatic route.

For the no pretreatment route, the treatment process is the main contributor to CED, GWP and WD, whereas pulp production contributes more to TA. Reduced electricity use during treatment is the most obvious way of reducing the environmental impacts of CNF from this route. However, this has been reported to be a challenge.[24,65]

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It should be noted that the CED seems to be a fair proxy indicator for the other environmental impacts, which has been suggested also by previous studies.[51,52]

3.2. Sensitivity Analysis and Scale-up Implications. The following aspects were identified as having a potentially strong influence on the results: (1) pulp production, (2) treatment electricity use, (3) transports, (4) ethanol production, (5) electricity mix, (6) heat source, and (7) solvent heat and material recovery. A sensitivity analysis based on what-if scenarios[66] was conducted to investigate their actual influence. Results are presented in Figure 3, and in more detail in the SI.

The influence of aspects 1−4 was tested in terms of a high impact scenario. Contrary to the baseline scenario, the high impact scenario employs the pulp production, treatment electricity use, transports, and ethanol production with the highest environmental impacts. This means sulphite pulp, 108 MJ/kg treatment electricity use for the no pretreatment route and 8.4 MJ/kg for the two other routes, transports from China and Russia (see the SI), and corn-based ethanol. As can be seen in Figure 3, there are some differences between the baseline and high impact scenarios. For the enzymatic route, the results increase 38% for CED, 110% for GWP, 130% for TA, and 12% for WD compared to the baseline scenario. For the carboxymethylation route, the results increase 18% for CED, 12% for GWP, 120% for TA, and 21% for WD compared to the baseline scenario. For the no pretreatment route, the results increase 52% for CED, 100% for GWP, 170% for TA, and 52% for WD compared to the baseline scenario. However, the positioning of the routes relative to each other remains.

Regarding aspects 5−6, the electricity and heat production chosen in the baseline scenario are representative for Swedish conditions but may not represent all countries or global averages. Assuming a fossil-based energy scenario, which means a coal-dominated electricity mix (modeled as Polish electricity, which has >90% coal) instead of the Swedish electricity and a light fuel oil boiler for heat production instead of a biomass boiler, some changes occur. Most notably, the GWP and TA for the enzymatic and no pretreatment routes increase (440% and 180%, and 1800% and 1700%, respectively, see Figure 3), which is mainly due to larger greenhouse gas and acidifying emissions from coal power. This highlights the importance of the choice of electricity mix, particularly for the no pretreatment route with its high use of electricity in the homogenization. But it should be noted that not even this radical change, from Sweden's hydro- and nuclear-based electricity to coal-based electricity, changed the relative positioning of the three routes.

Regarding aspect 7, there are considerable amounts of waste heat in the Ecoinvent data set from waste solvent incineration—about 20 MJ heat per kilogram of solvent waste. This heat could potentially be recovered and would then replace heat from the biomass boiler and reduce the environmental impacts of the carboxymethylation pretreatment. Such a scenario was considered and is called "solvent heat recovery" and is also shown in Figure 3. The CED is reduced by 33% due to solvent energy recovery and TA by 41%, while the other impact categories remain similar to the baseline scenario.

Solvent material recovery may be another possibility. However, ethanol and isopropanol have similar boiling points (78 and 83 °C) and volatilities, which make separation through distillation difficult, although extractive distillation may be an option.[67,68] Both isopropanol and ethanol also form azeotropes with water, and water is formed, albeit in low amounts, when the hydrochloric acid formed during carboxymethylation is neutralized with sodium hydroxide. The enthalpies of vaporization, which would be the minimum amount of energy required to conduct a separation based on distillation, are approximately 0.8 MJ/kg for ethanol and 0.7 MJ/kg for isopropanol. Together, this gives an approximate energy requirement of 20 MJ/kg CNF, which is much less than the life cycle energy use of these materials per kilogram of CNF. This indicates that there is theoretically a potential reduction in energy use, and thereby also other impacts, from solvent material recovery in the carboxymethylation route. We therefore suggest future research to investigate the technical feasibility and environmental impact of solvent material recovery in this route.

Gavankar et al. discussed the role of time and scale for LCA studies of emerging technologies and suggested the use manufacturing readiness levels (MRL) as an indicator of technological maturity.[69] The CNF production studied here corresponds approximately to a MRL of 8−9, which means small or pilot scale production. Gavankar et al. showed that substantial environmental improvements occur between a MRL of 8−9 and 10 for the case of carbon nanotubes, including reductions in GWP of 80−90% due to more efficient use of the feedstock.[69] However, CNF feedstock yield is already high (effectively 1). The main reductions in environmental impacts from scale up should be from reduced use of solvents in the carboxymethylation pretreatment, reduced use of electricity in the treatment processes, and reduced use of water for washing in the enzymatic and carboxymethylation pretreatments. This has already been recommended in this study.

3.3. Comparison to Other Carbon Nanomaterials. In this section, the results for CNF from this study are compared to previous results for CNF and CNC. They are also compared to LCA results for carbon nanotubes and graphene, which are materials that can also be used as reinforcement in composite materials, thereby fulfilling the same function.

In the study by Li et al., CED results as low as about 1000 MJ/kg were obtained for modeled industrial production of CNF by TEMPO oxidation and homogenization.[33] Results as high as 18 000 MJ/kg were also obtained for lab-scale production of CNF by chloroacetic acid etherification pretreatment with sonication treatment. The main reason for this high number is that Li et al. assumed a higher input of ethanol and isopropanol in their pretreatment process than Wågberg et al. (Table S2) and that they did not include any solvent recovery (neither heat nor material recovery).[33,49]

In the LCA of CNC by de Figueirêdo et al., results obtained were 1800−16 000 MJ/kg for energy use, 120−1100 kg CO_2 eq/kg for GWP, and 140 m^3/kg for WD.[34] Although it is uncertain if their energy use indicator is comparable to the CED, only the highest CED result from this study (for the carboxymethylation route) is of the same order of magnitude as their lowest energy use result. For the other environmental impacts, the results of de Figueirêdo et al. are much higher.

Gavankar et al. reviewed energy use for carbon nanotubes and found it to be in the approximate range of 1000 to 1 million MJ/kg depending on technological maturity.[69] For graphene, Arvidsson et al. calculated an energy use (similar to CED) of 72−1100 MJ/kg and a blue water footprint (similar to WD) of 0.48−13 m^3/kg.[10] Pizza et al. calculated the primary energy use of graphene (similar to CED) to be 1900 MJ/kg.[70]

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This comparison indicates that CNF produced by the three routes studied in this paper generally have low per-kilogram environmental impacts compared to carbon nanotubes, and impacts of similar magnitude as graphene.

3.4. Implications and Future Studies. The results of this study show that the carboxymethylation route has the highest environmental impacts. The main recommendation from this study to CNF producers and researchers is therefore to pursue the two other production routes studied here if they want to reduce environmental impacts of CNF. Alternatively, they could try to reduce the amount of solvents per kilogram of CNF for the carboxymethylation route, either by solvent recycling or by reducing the input. The comparison to the results reported by Li et al. indicated that the environmental impacts of CNF from the enzymatic and no pretreatment routes were lower than those of CNF produced by TEMPO oxidation and homogenization.[33] Future studies comparing these routes further would be of interest, especially considering the current high interest in TEMPO oxidation in the field.[22] Environmental studies of additional pretreatment processes combined with homogenization or microfluidization would also be interesting. Such pretreatment processes include acetylation[22] and the adding hydrophilic polymers (such as carboxymethylcellulose).[24]

It would also be interesting to conduct LCA studies that include CNF use and end-of-life, that is, studies with a cradle-to-grave scope. Kim and Fthenakis noted that although many nanomaterials were energy-intensive in cradle-to-gate studies, they can typically provide reduced cradle-to-grave energy use to nanomaterial-containing products.[14] For example, Khanna and Bakshi showed that polymers reinforced with carbon nanofibers had higher cradle-to-gate energy use than steel, but the use of the nanofiber-reinforced polymers in automobiles resulted in lower energy use compared to steel.[71] Field emission displays containing carbon nanotubes were shown to have lower or similar environmental impacts as conventional displays due to increased viewing lifespan.[20] Studies comparing conventional composite materials to composite materials containing CNF or other nanomaterials (such as carbon nanotubes and graphene) would be interesting to conduct, especially for the enzymatic and no pretreatment routes that already have comparatively low environmental impacts. Similarly, comparative LCA studies of conventional transparent films and films containing CNF would be interesting.

■ ASSOCIATED CONTENT

Supporting Information

SI Section 1: Phosphate buffer calculations. SI Section 2: Sodium bicarbonate calculations. SI Section 3: Transport calculations (including Table S1). SI Section 4: Heat loss calculations. SI Section 5: Comparison of input materials (including Table S2). SI Section 6: Tables showing detailed results of the sensitivity analysis (including Tables S3−S6). SI Section 7: Table showing included background processes with data sources (including Table S7). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00888.

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Notes

The authors declare no competing financial interest.

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