ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

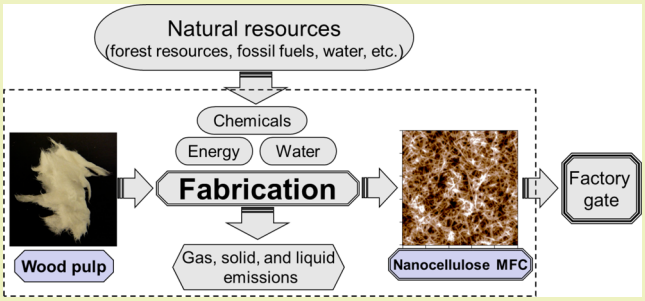
Nanocellulose Life Cycle Assessment

Qingqing Li,[†] Sean McGinnis,[‡] Cutter Sydnor,[§] Anthony Wong,[‡] and Scott Renneckar*,[†]

[†]Department of Sustainable Biomaterials, [‡]Department of Material Science and Engineering, and [§]Department of Civil and Environmental Engineering, Virginia Tech, Virginia 24061, United States

Supporting Information

ABSTRACT: Nanocellulose is a nascent and promising material with many exceptional properties and a broad spectrum of potential applications. Because of the unique and functional materials that can be created using nanocellulose, pilot-scale development for commercialization has begun. Thus a thorough understanding of its environmental impact, covering the whole life cycle of nanocellulose, becomes the foundation for its long-term sustainable success. In this current study, four comparable lab scale nanocellulose fabrication routes were evaluated through a cradle-to-gate life cycle assessment (LCA) adopting the Eco-Indicator 99 method. The results indicated that, for the chemical−mechanical fabrication routes, the majority of the environmental impact of nanocellulose fabrication is dependent upon both the chemical modification and mechanical treatment route chosen. For sonication, the mechanical treatment overshadows that from the chemical modifications. Adapting the best practice based on unit mass production was 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation followed by homogenization, as TEMPO oxidation resulted in a lower impact than carboxymethylation. Even though the fabrication process of nanocellulose presents a large environmental footprint markup relative to its raw material extraction process (kraft pulping), it still exhibits prominent environmental advantages over other nanomaterials like carbon nanotubes.



KEYWORDS: *Nanocellulose, Life cycle assessment, Environmental impact, Sustainable, TEMPO oxidation, Sonication, Homogenization*

INTRODUCTION

The commercialization of nanocellulose is forthcoming with the projected GPD of $600 billion worldwide by 2020;[1,2] hence it is critical that we understand how much environmental impact the fabrication process will generate and design the best manufacturing system accordingly. Life cycle assessment (also known as life cycle analysis (LCA)) can be used for evaluating the cumulative environmental impact associated with all stages of fabrication of materials from the initial extraction of raw materials (cradle) through the end-of-life disposal of final products (grave).[3−7] LCA enables the selection of best fabrication methods with quantified indexes (LCA scores) related to environmental impact.[3−5] LCA requires careful goal and scope definition in order to define the objectives, the functional unit, and the system boundaries. On the basis of the systems boundaries, a life cycle inventory (LCI) is compiled that documents and quantifies inputs and outputs related to the material and energy flows. Life cycle impact assessment (LCIA) then transforms the inventory data into comparable values in selected environmental impact categories. On the basis of the data analysis, meaningful insights and decisions can be made to minimize the environment impact of products and processes.[4]

Cellulose is a naturally occurring biopolymer and has been recognized for its many environmentally friendly characteristics, such as biodegradability and biocompatibility.[8−12] Cellulose exists in a supramolecular structure in its native state, with the individual polymer chains assembled together in fibrils of a few nanometers in cross-section, with dimensions dependent on plant type. Isolated cellulose with at least one dimension in the nanometer range (usually below 100 nm) which exhibits novel properties associated with its size is referred to as nanocellulose.[9,13] Nanocellulose is used in many material applications such as polymer reinforcement[14,15] and transparent films.[16−19] Nanocellulose can be prepared through many different approaches, which can be classified into two general categories: top-down and bottom-up.[8,20] The top-down approaches, which obtain nanocelluloses by extracting cellulose particles from various sources,[21] typically involve intensive mechanical and/or chemical treatments to deconstruct the intrinsic native structures from the plant cell wall. Top down approaches can be further divided into three subcategories: mechanical, chemical, and chemical−mechanical. The bottom-up approaches assemble cellulose nanostructures either from the solution state of cellulose molecules or utilize biosynthesis processes.[9,20] On the basis of the preparation methods and raw material origin, nanocelluloses are conventionally classified into three subcategories (Figure 1): (i) microfibrillated cellulose (MFC), an elongated fibril form of nanocellulose, is prepared

Received: January 29, 2013
Revised: April 23, 2013
Published: May 22, 2013

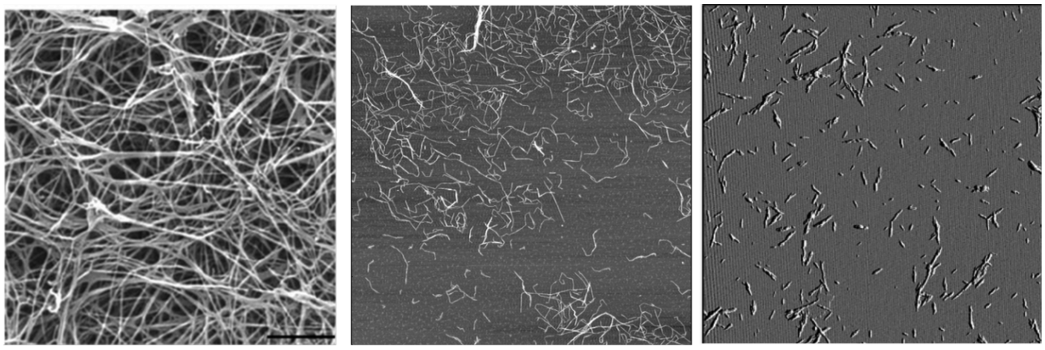


Figure 1. Images of different types of nanocelluloses. Reprinted with permission from refs 9 and 24. Copyright 2011 John Wiley and Sons and 2007 American Chemical Society.

from wood and other plant fibers via chemical, mechanical, or combined treatments; (ii) nanocrystalline cellulose (NCC; cellulose nanocrystals, crystallites, and whiskers) is a rodlike highly crystalline form of nanocellulose, prepared from a broader range of raw materials including plant-, animal-, or bacteria-originated cellulose via acid hydrolysis; (iii) bacterial nanocellulose or BNC (a.k.a.: bacterial cellulose, microbial cellulose, biocellulose), is a network form of nanocellulose, produced by certain bacteria.[9,22,23]

Nanocelluloses have developed applications across a number of markets and thus will have an increasing impact on consumer, health, food, and industrial goods. MFC finds its applications in paper making as reinforcement agents or functional coatings (e.g.: grease proofing or moisture absorbing), and in food, cosmetic, pharmaceutical, and hygiene products as the emulsion and/or dispersion additives, as well as in various nanocomposites and films as structural components. All these applications are built on MFC's unique combination of properties: surface functionality, water retention, large aspect ratio, large specific strength, rheology, and optical characteristics, as well as its universal compatibility with natural and biological environment.[8,9,13,23] As for NCC, the most readily implementable applications are based on mechanical properties which allow use as a reinforcement agent in composite films to increase strength.[8,9,12,24] This form of nanocellulose also shows potential applications in nanomedicines.[24,25] BNC has many properties that set it apart from MFC and NCC such as it forms a stable nanofiber network, has shapability during biosynthesis, exhibits excellent mechanical strength while maintaining high flexibility, and has been proven to be noncytotoxic and nongenotoxic.[9] These properties lead to BNC use in novel application fields like food gels, artificial blood vessels, wound dressing material, fuel cell membranes, and even films for electronic appliances.[9] An example of the successful commercialization of BNC in food industry is the Nata de coco—a jelly like food product produced via *Acetobacter xylinus* fermenting in coconut milk.[26]

MFC is one of the most widely studied nanocelluloses prepared from different approaches including: pure mechanical treatment or combined chemical-mechanical treatment (chemical pretreatment followed by mechanical agitation). First described by Turbak et al. in 1983, homogenization processes different types of pulps with intensive shear treatments with controlled pass numbers through a small orifice at high pressure.[23,27] The predominant end product has a netlike structure, with a diameter ranging from 25 to 100 nm in the dry state. Because releasing nanocellulose from native cellulose fibers requires the disruption of the hydrogen bonding system, the energy consumption is relatively large (27 000 kW h/t), which becomes the major impediment of its commercial success.[9,23] Sonication is another technique to overcome the interfibril bonds within pulp fibers. The first work to produce MFC with mechanical agitation method was reported by Wuhrmann et al. in 1946, where plant fibers from ramie, hemp, and cotton were subjected to intensive sonication treatment and fine fibrils (6−7 nm width) were yielded solely as a function of the mechanical agitation intensity.[28] Inspired by Wuhrmann's work, many groups have employed sonication as a major avenue to isolate nanocellulose.[15,16,29−33] Different chemical pretreatments (e.g.: oxidation,[32] carboxymethylation,[16,34] acid hydrolysis,[35] and enzymatic hydrolysis[36]) and mechanical agitations (e.g.: sonication, homogenization, blending, etc.), as well as their different combinations have been extensively investigated to generate MFC.[12,37] The most common chemical−mechanical approach is to modify the cellulose fiber surface via carboxylation or carboxymethylation reactions (e.g.: TEMPO oxidation,[38] chloroacetic acid etherification[34]) to introduce negative charges onto the microfibril surface allowing easy separation; the modified fibers are subjected to mild to intensive mechanical treatments to liberate MFC from the raw materials.[37] The end product, MFC, is in long fibril forms with lateral dimensions of single digit nanometers (or even subnanometers) and hundreds of nanometers to several micrometers in length.[30,39]

Given all the promising applications, however, the commercialization of the MFC nanocellulose is still in its early stage.[1,2,8,12] The general consensus for the next stage of development is to continue exploring a broader marketplace beyond the conventional "stronger and stiffer" structural reinforcement application,[8] as well as to address the high energy consumption and capital cost for industrial scale production.[9] Therefore, comprehensive LCA for nanocelluloses (especially the energy consumption analysis during production) are an essential step in their commercialization efforts as well as enhancing this emerging industry's responsible and sustainable development. Besides the energy consumption issue, there is also the tendency to assume that nanocellulose should share the same favorable environmental impact as its precursors, such as wood pulp, since the nanoscale particles are isolated directly from cellulose.[9,13,20] However, the processes of isolating

nanocellulose via chemical modifications and mechanical disintegrations can involve polluting or toxic chemicals and energy intensive steps,[27] which may produce significant environmental burdens and may neutralize or even overshadow the inherent environmental benefits using cellulose.

LCA can be utilized to gauge the cumulative environmental impact associated with the nanocellulose fabrication process, reveal the relative environmental footprint compared to its precursor raw material, and provide a quantitative reference to assess the environmental attributes of different nanomaterials that serve similar applications (i.e., polymer reinforcement). To the best of our knowledge, only one LCA report has been released considering environmental impacts of nanocellulose.[40] In this report, a cradle-to-gate LCA for nanofibrillar cellulose (NFC) was done using the impact assessment RECIPE to provide values for climate change potential, eutrophication, terrestrial acidification, and fossil fuel depletion. This LCA used a combination of lab and pilot scale measurements, estimates, and expert opinions to look at three different processing routes, including TEMPO-oxidation with homogenization that is similar to one route (TOHO) in this work. It is not clear if this report was peer-reviewed, and the sources for the quantitative inventory data which serves as the basis for the LCA are not detailed.

Although many fabrication methods/routes have been suggested and practiced in a lab setting, there are only the quantitative environmental impact values available from this paper, which makes further improvement difficult. Therefore, LCA can be used to guide the emerging fabrication technologies toward reducing environmental impacts,[41] and the data collected at laboratory scale provides important insights for the large scale industrial production in the absence of industry data and analysis.

In this LCA, four comparable chemical−mechanical approaches for lab scale nanocellulose fabrication (TEMPO-oxidation followed by sonication or homogenization and chloroacetic etherification followed by sonication or homogenization) were examined with the Eco-Indicator 99 impact assessment method.[42] The overall environmental impacts across these fabrication routes were quantified using this method. This LCA research attempts to provide insights to at least the following two questions:

(1) Under typical laboratory scale conditions, what nanocellulose choices lead to the lowest environmental impacts?
(2) On the basis of lab-scale LCA results, what additional questions and analysis are necessary to provide useful information to decision makers who want to consider the environmental impact of nanocellulose production at the industrial scale?

EXPERIMENTAL SECTION

LCA Scope and Functional Unit Definition. The system boundary of this LCA is shown schematically in Figure 2. This boundary defines a "cradle-to-gate" analysis since it includes the extraction of the raw materials for chemical precursors and energy as well as the processing of the nanocellulose but not the use or disposal phase of the nanocellulose which would be different for every application. "Cradle-to-gate" LCAs are common boundaries for materials which are used in a wide variety of applications. This boundary includes the steps associated with the nanocellulose fabrication, starting from delignified kraft pulp, followed by chemical modification, mechanical disintegration, and purifying, until the final product nanocellulose is ready to deliver at the "factory gate".

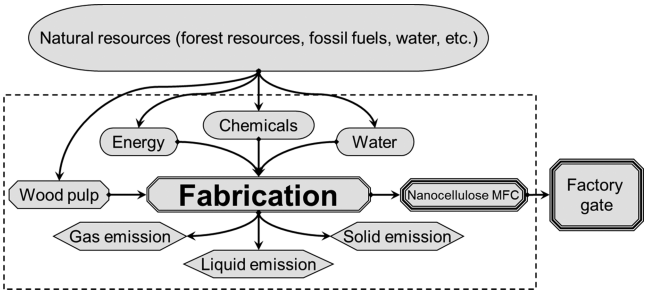


Figure 2. Cradle-to-gate LCA system boundary (indicated by the dashed line box) of lab-scale nanocellulose fabrication.

The system inputs considered in this analysis include are wood pulp, direct processing energy (in the form of electricity), chemicals, and water. Many of these inputs are based on compiled LCA processes, and therefore, the analysis includes extensive upstream accounting for associated raw materials and energy. The corresponding outputs were final product nanocellulose, disposal of process wastes, and emissions related to upstream processing of raw materials and energy production. Other than the transportation which is included in the upstream processes for kraft pulping, all transportation of raw materials to the lab has been excluded since it is similar for all cases. Process equipment manufacturing was also excluded since the lab scale equipment is used for many processes and the contributions are considered negligible over the life of the equipment.

The LCA functional unit must be selected carefully to allow for fair comparisons of the processes. For this case, the functional unit is defined as 10 g equivalent dry mass of the end product nanocellulose at the factory gate. All reference flows of materials and energy are scaled appropriately for the production of this amount of nanocellulose.

Nanocellulose (MFC) Fabrication Process Description. The nanocellulose fabrication routes evaluated in this LCA are presented in Figure 3. Fabrication comprised a chemical modification process, a mechanical disintegration process, and a centrifuge purifying process (only for sonication treated samples). Two comparable methods for both chemical modification and mechanical disintegration processes were selected. The starting material, delignified kraft pulp (kindly donated by Weyerhaeuser Company), was converted to nanocellulose.

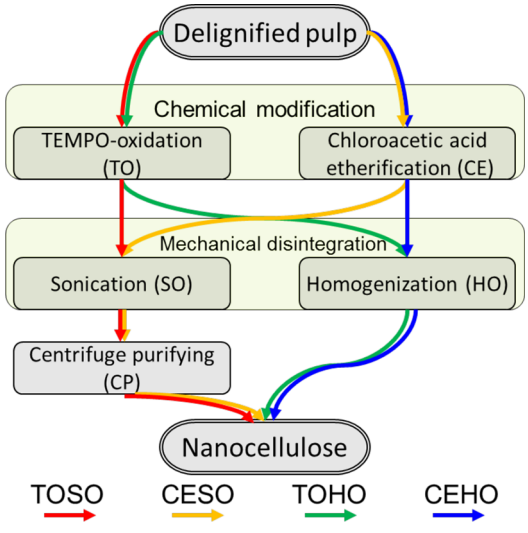


Figure 3. Cellulose MFC fabrication process flow, with colored arrows indicating 4 distinct pathways: red—TOSO, yellow—CESO, green—TOHO, and blue—CEHO.

dx.doi.org/10.1021/sc4000225 | ACS Sustainable Chem. Eng. 2013, 1, 919−928

As a result, four different fabrication routes were designed (Figure 3): the first route is TOSO (TEMPO-oxidation for chemical modification, sonication for mechanical disintegration), the second route is TOHO (TEMPO-oxidation for chemical modification, homogenization for mechanical disintegration), the third route is CESO (chloroacetic acid etherification for chemical modification, sonication for mechanical disintegration), and the fourth route is CEHO (chloroacetic acid etherification for chemical modification, homogenization for mechanical disintegration). Primary data for TEMPO oxidation was collected directly from the lab for this study, while the chloroacetic acid modification relied on previously reported inputs.[34]

Chemical and Mechanical Processes Descriptions. *Chemical Modification Process, TEMPO Oxidation (TO).* Delignified kraft pulp was oxidized following previously reported techniques with the key parameter controlling oxidation of NaClO at 5 mmol per gram of dry fiber.[30] System inputs included: 10 g equivalent dry mass of kraft pulp, 0.06 g of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2.4 g of sodium bromide (NaBr) powder (in inventory NaBr is substituted for molar equivalent of NaCl), 21.4 mL of sodium hypochlorite solution (13% w/w concentration), 50 mL of 0.5 N sodium hydroxide (NaOH) solution (for controlling the pH environment), 5.5 L of deionized water (0.5 L for reaction and 5 L for washing), 200 mL of ethanol (for quenching the reaction), and electricity to power the experiment equipment (overhead blender, syringe pump, and pH meter). System outputs were surface modified pulp (oxidized cellulose, intermediate product) and liquid emissions.

Chemical Modification Process of Chloroacetic Acid Etherification (CE). Delignified kraft pulp was dispersed in aqueous suspension, and then, aqueous NaOH and chloroacetic acid were added into the system in sequence to activate the reaction at 60 °C. The reaction was stopped by cooling down to room temperature and adjusting the pH to neutral range after 2 h.[34] System inputs included 10 g equivalent dry mass of delignified kraft pulp, 1.41 g of NaOH powder, 2.12 g of chloroacetic acid powder, 5.12 L of deionized water (0.12 L for reaction and 5 L for washing), 435 g of isopropanol, and 262 g of ethanol. System outputs were surface modified pulp (carboxymethylated cellulose, intermediate product) and liquid emissions.

Mechanical Disintegration Process by Homogenization (HO). Chemically modified pulp was processed with high-pressure homogenizer (Mini DeBEE) under 205 MPa for 2 passes to produce nanocellulose. System inputs were chemically modified pulp and electricity and the output was end-product nanocellulose. The 10 g functional unit of nanocellulose was derived from four batches, processing 2.5 g per batch, equivalent to a concentration of 0.5% in 500 mL DI water. A processing rate of 200 mL/min was measured and working power of 2.87 kW measured from the ammeter.

Mechanical Disintegration Process by Sonication (SO). Chemically modified pulp was subjected to intensive sonication treatment (a 19 mm diameter horn was used to sonicate the modified pulp at 20 kHz, VC700, Sonics & Materials) for designated time intervals (30 min for this LCA) to produce nanocellulose. System inputs were chemically modified pulp and electricity (power consumption measured by equipment read-out measured in kilojoules for the time intervals and converted to kilowatt hours); output was unpurified nanocellulose (with titanium impurities from the sonication process). Batch size is defined as 0.3 g/batch, equivalent to a concentration of 0.1 g wt % in 300 mL DI water. After sonication, nanocellulose was purified by centrifugation (15 min @ 5000 rpm, Eppendorf centrifuge 5804) to remove the titanium particle impurities introduced during the sonication . System inputs were unpurified sonicated nanocellulose suspensions and electricity (measured with Kill-A-Watt meter) while outputs were end product nanocellulose, solid, and liquid emissions.

Key Assumptions. The following assumptions were made to facilitate the LCA models of nanocellulose from the above laboratory practices. In some cases, small changes in LCA assumptions can have large impacts on the results while in other cases the results can be insensitive to assumptions. For those LCA results which were thought to be sensitive to the assumptions, we performed scenario analysis with different assumptions.

1. Kraft pulp (starting material) loss during the fabrication process is negligible. The material mass balance indicated that although weight loss may occur during the washing, transferring, and purifying steps, the total weight loss is below 3%. For simplicity, we assume this weight loss exerts no significant influence to the LCA results.
2. The two chemical modification processes (TO and CE) produce comparable surface charged cellulose fibers. The TO modified pulp is carboxylated cellulose (with C6 converted to carboxyl group, average degree of substitution (DS) ∼ 0.23) while CE modified pulp is carboxymethylated cellulose (with primary hydroxyl groups converted to carboxymethyl group, DS ranges from 0.10 to 0.20), so the chemical structures are slightly different and degrees of substitution are also different.[10,16] However, both modified pulps are similar in the sense that the modification processes introduce anionic surface charges onto the pulp while maintaining the primary physical and mechanical properties of the isolated nanocellulose.
3. The two mechanical disintegration processes (SO and HO) produce comparable nanocellulose and are independent of the previous chemical modifications. Both processes deconstruct surface modified pulp into disintegrated nanocellulose. However, due to the different mechanisms as well as the starting materials (carboxylated cellulose vs carboxymethylated cellulose), the products could be different in dimension distributions, surfaces charges, and the associated bulk properties. We assume these differences are insignificant for most of the downstream applications.
4. Batch processing capacities of homogenization (HO) is assumed to be three times of that of sonication (SO). The batch processing capacities for both HO and SO can vary in certain ranges, dependent on the target concentration of the nanocellulose and the batch volume limits of the equipment. Therefore for 10 g (the functional unit) of dry nanocellulose, it takes 4 batches processed via HO (2.5 g/batch or 0.5 wt % in 500 mL DI water) and 33 batches via SO (0.3 g/batch or 0.1 wt % in 300 mL DI water). Also, since SO processed nanocellulose has to go through the centrifuge purifying (CP) to remove the titanium impurities, it requires 33 batches of SO plus an additional 33 batches of centrifugation to process 10 g of nanocellulose.
5. The common procedures (e.g.: washing) do not influence the comparison among four fabrication routes and are therefore considered negligible to simplify the analysis.
6. The LCI process data assumes ethanol is manufactured from the fermentation of biomass (corn). Ethanol is also commonly produced from hydration of ethylene with the process of choice depending on the relative cost of the two processes. A conversation with the supplier of the lab's ethanol confirmed that the ethanol was produced from corn, but the scenario of ethanol from ethylene was modeled for comparison.
7. Liquid processing wastes were mixed with other laboratory wastes and disposed through the university as hazardous liquids. These were modeled as incinerated or combusted liquid waste for energy recovery as is a common practice for laboratory wastes. The emissions from this incineration/combustion were included in the analysis, but transportation of the wastes and the energy recovery was not modeled due to complexity. Both of these processes emit chemicals into the atmosphere, but the energy recovery offsets this to some degree since another energy source is displaced.
8. Solvent evaporation was considered negligible, and these direct emissions were not included.

Life Cycle Inventory Analysis (LCI). All the data used in this LCA comes from the following four sources: original data, literature data,[34] SimaPro databases, and estimations. Inventory details are provided in the Supporting Information Tables 1−4.

Foreground Data.

1. For chemical processing, all the input and output (emissions) data were scaled to the equivalent amount for producing 10 g dry nanocellulose (the functional unit). The direct energy input in the form of electricity during the chemical processes (i.e.: overhead stirring system, heating plat, pH meter, centrifuge washer, cooling system, etc.) was measured with an electricity usage monitor (P4400 Kill A Watt, P3 International); three readings were taken to get the average value in kilowatt hours.
2. For mechanical processing, electricity was the only direct input. The electricity consumption was calculated based on the operation time and the equipment power specifications.

Background Data. The upstream manufacturing data for kraft pulp, chemicals, water, and electricity are modeled using the inventory database provided within SimaPro version 7.3 (Ecoinvent v.2, USLCI v1.6.0). The specific processes are also listed in the Supporting Information Tables 1−4. Although inventory data from the US would be preferable for these processes, many of the chemicals and raw materials were not available from the USLCI database. Commodity chemicals are often produced with similar technology throughout the world and often sourced outside the US, so the European data was considered acceptable despite some differences in fuel sources for electricity generation. Process data from EcoInvent has the advantage that these processes are consistent with one another with regard to boundary conditions which can lead to inaccuracies if LCI process data from different databases was used.

Electricity for lab scale processing was a low-voltage average for the US grid (approximately 57% coal, 22% nuclear, 17% natural gas, and 4% others) from the USLCI database which included typical line losses. This data is representative of the year 2000 fuel mix, so the recent shift away from coal due to displacement by natural gas is not considered but would be the same for all four cases compared in this study. While this is a good general case for this LCA, interpretation of these results for a specific location should consider the current electricity fuel source mix compared to this average.

Estimations. For some process data (e.g., the volume for the tap water used in washing the intermediate product), we estimated the value from experience and estimated the uncertainty in these cases to be approximately 10%. Additionally, there are two key reactants in the TEMPO oxidation process that were not available in existing LCI databases. TEMPO was not included in the inventory because very limited information about its environmental impact (or immediate precursor chemicals) is available. Moreover, it comprises much less than 1% of the mass flows in the process. NaBr, not available in any of the SimaPro databases, was replaced with NaCl for impact estimation, because the two chemicals share many similarities in the industrial manufacturing processes and environmental outputs.[43,44] Both TEMPO and NaBr could be modeled more accurately in the future if evidence suggests the associated impacts are significant.

RESULTS AND DISCUSSION

Life Cycle Impact Assessment (LCIA). LCA results depend critically on the impact assessment method used. These methods use different scientific models to translate the inventory amounts into environmental impacts using characterization factors. Several impact assessment methods were used in this analysis.

Energy use is a metric that is well understood and often reported, but it is not strictly an environmental impact. However, energy use is strongly correlated with both the use of raw materials as well as emissions. Cumulative energy demand (CED, SimaPro v1.08) was used obtain the overall energy use across the life cycle.[45] CED has been shown to correlate strongly with other environmental metrics calculated from a wide range of different impact assessment methods.[46] The CED method further breaks down energy use into the categories of nonrenewable (fossil, nuclear, and biomass) and renewable (biomass, solar/wind/geothermal, and hydro) energy. The units for CED are megajoules (MJ).

Global warming potential (GWP) is also a frequently reported environmental metric due to both the strong scientific consensus on the potential implications of this issue as well as the corresponding societal, political, and economic ramifications. This impact was modeled using the International Panel on Climate Change method (IPCC 7 GWP 100a v1.02) which has a time frame of 100 years.[47] This method uses the midlevel time horizon, but there are also 20 and 500 year methods which account for differential lifetimes of greenhouse gases in the atmosphere. The units for IPCC 7 GWP are kilograms CO_2, equivalent.

While energy and climate change are the most often quantified environmental impacts, LCA methods allow for a much wider range of environmental impacts to be quantified. Eco-Indicator 99 (EI99, SimaPro v2.08) was used to provide an end point damage assessment using the 11 impact categories shown in Table 1[42] EI99 translates environmental impacts into

Table 1. Environmental Impact Categories Considered in Eco-Indicator 99[42]

environmental impacts	end point categories
carcinogens	human health
respiratory organics	
respiratory inorganics	
climate change	
radiation	
ozone layer	
ecotoxicity	ecosystem quality
acidification/eutrophication	
land use	
minerals	resources
fossil fuels	

"Points (Pts)" under three comprehensive end point categories: human health, ecosystem quality, and resources. The values can then be normalized, weighted, and reported collectively as one single score for comparison.[42,48,49] In this method, higher scores represent larger environmental impact. The EI99 method is "easy to understand but there is the risk of losing transparency".[48] The single scores reported using EI99 are dimensionless values, normalized to the overall annual environmental load per capita, in continental Europe.[42] EI99 normalization values were not available in SimaPro for the US, but this is not a critical issue in the comparisons of this study since each option was normalized by the same values. EI99 also provides detailed breakdowns of the impact values in either the 3 end point categories or 11 environmental impact categories of Table 1.

EI99 also has three weighting sets reflecting different perspectives for gauging the environmental damage—the egalitarian (E), hierarchist (H), and individualist (I) perspectives.[42] These weights are necessary to obtain single score comparisons but are subjective unlike the LCI and normalization values in the models. We ran our models using all three perspectives, but the baseline model will use the hierarchist weighting which uses a midlevel time frame and risk perspective. The values for the end point categories for the three weighting schemes are shown in Table 2. Also note that these three EI99 methods have, for some categories, different

Table 2. Weighting Values for EcoIndicator Methods[24]

EcoIndicator method	time horizon	intergenerational responsibility	human health	ecosystem quality	resources
individualist (I)	short	present > future	55%	25%	20%
hierarchist (H)	medium	present = future	30%	40%	30%
egalitarian (E)	long	present < future	30%	50%	20%

characterization factors to take into account the different perspectives.

Baseline Comparison of Four Processing Methods. CED and GWP impact values for the four baseline processes are shown in Table 3. Sonication (SO) requires more energy than homogenization (HO), and the chloroacetic acid—etherification route (CE) is more energy intensive than the TEMPO-oxidation route (TO). Recall that sonication requires a follow-up centrifuge step for purification and the CE process uses both isopropanol and ethanol, while TO process only uses ethanol. Details of the four process inventories are included in the Supporting Information Tables 1−4.

Table 3. CED and GWP Results for 10 g Nanocellulose Production

impact category	CEHO	CESO	TOHO	TOSO
CED total energy (MJ)	64.9	176.1	34.7	145.9
CED nonrenewable energy (MJ)	48.8	160	19.5	130.6
CED renewable energy (MJ)	16.1	16.1	15.2	15.2
CED chemical process (MJ)	54.4	54.4	24.2	24.2
CED mechanical process (MJ)	10.5	121.7	10.5	121.7
IPCC7 GWP 100a (kg CO_2, equiv)	3.6	11.6	1.9	9.8

Overall, TOHO requires the least energy across the entire process life cycle. More than 97% of the nonrenewable energy for these processes is categorized as fossil-derived while a similar percentage of the renewable energy is categorized as biomass. In this baseline case, the renewable biomass energy comes from the corn fermentation process for the manufacturing of the ethanol.

The GWP values follow the same trend as the energy demand for these processes since most of the greenhouse gas emissions are dominated by carbon dioxide and result directly from the use of fossil fuels for energy. These climate change values are the only ones that can be compared easily to the results from the previous LCA on NFCs. For the 3 processes and 2 electricity generation scenarios studied in the previous work by Hohenthal, et al., the GWP values range from 0.7−3.0 kg CO_2 equiv/kg nanocellulose.[40] From the data in Table 3, the GWP values for this study range from 190 to 1160 kg CO_2 equiv/kg nanocellulose. It is clear that the electricity inputs for the Hohenthal et al. LCA have orders of magnitude less direct electricity input per unit nanocelluose mass than in this work. It is interesting to note in the Klemm et al. review a number examples are provided for relative energy consumption with the value of 27 000 kW h/ton cited for the nonmodified kraft pulp and 500 kW h/ton for the carboxylated pulp.[9] Processing time, concentration, number of passes, and power consumption are key variables in these systems that dictate energy demand in the fibrillation step. Homogenizers that use high pressure to shear the solution through a small orifice are limited by the concentration throughput because of clogging issues. An increase of an order of magnitude of concentration in our study would reduce the total energy demand to ∼10 000 kW h/ton for our two pass scenario at 250 mL/min. This number is similar to the Hohenthal et al. report where they use a 4% concentration in their LCA combined with a single pass homogenization step to derive the 4900 kW h/ton energy estimate. In Supporting Information Table 5, we present several different scenarios for energy consumption related to the energy cost of the homogenization step per pound of material. As can be noted, in our lab system the energy cost of mechanical fibrillation is just under $3 USD per pound of nanocellulose, which demonstrates the large amount of energy required for this lab scale process.

The total energy demand for these processes was also broken down into chemical and mechanical process components in Table 3. The chemical energy corresponds to the energy for all the raw materials and energy in the chemical synthesis of the nanocellulose (CE or TO). The mechanical energy corresponds to the energy used in the sonication/centrifugation or homogenization step (SO or HO) for these processes. As shown graphically in Figure 4, the mechanical processes for sonication demand a larger fraction of the energy than for the homogenization processes. For the homogenization processes, the chemical processes have greater energy demand than the mechanical process. This distribution of energy is an important consideration for industrial scale-up options for these processes demonstrate that sonication does not appear to be competitive with homogenization.

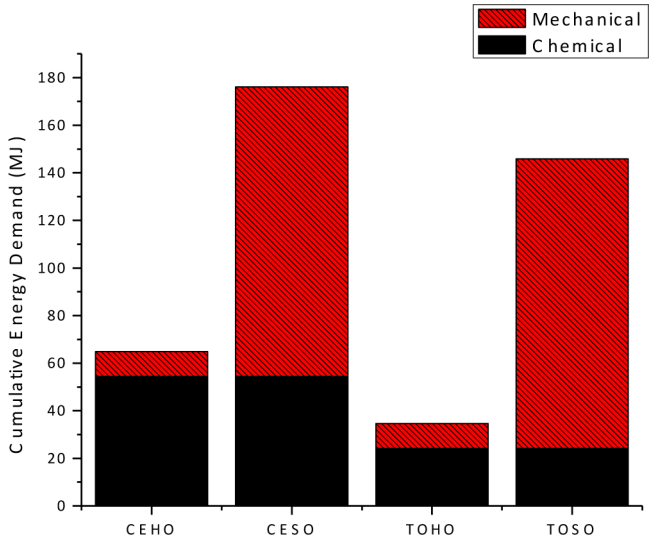


Figure 4. CED values for nanocellulose production routes separated into mechanical and chemical processes.

In addition to the energy and climate change impacts, EI99 single scores are shown in Table 4 with a breakdown by end point category detailed in Figure 5. The SimaPro network diagrams for these models at a cutoff level of 5.5% shows the LCA models visually in the Supporting Information Figures 1−4.

Despite the LCA model, differences from a short-term individual perspective (I) to a long-term societal perspective

Table 4. EI99 Results for Nanocellulose Production Routes with Different Impact Method Perspectives

method	CEHO	CESO	TOHO	TOSO
Eco-Indicator I/I (Pt)	0.23	0.73	0.15	0.65
Eco-Indicator H/H (Pt)	0.35	0.78	0.16	0.60
Eco-Indicator E/E (Pt)	0.30	0.84	0.18	0.72

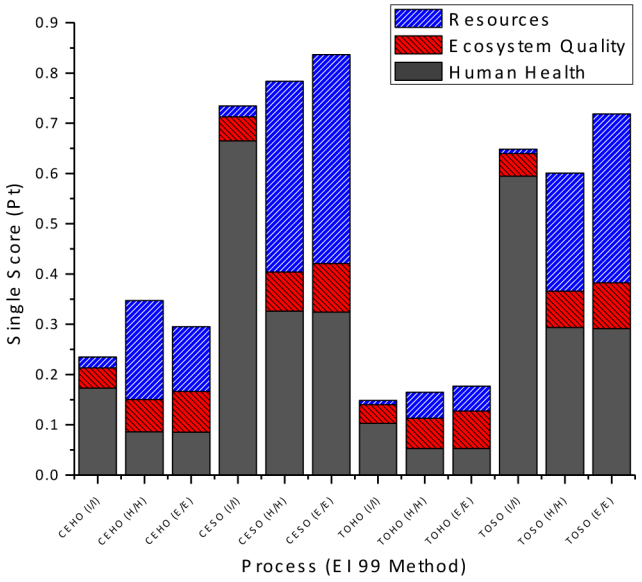


Figure 5. Single score impact factor for the four fabrication methods, and three different impact factor perspectives.

(E), the order of environmental impacts stays the same from TOHO (lowest in each perspective) to CEHO to TOSO to CESO (highest in each perspective). Note also that this is the same result obtained from the energy and climate change models despite the inclusion of nine more impact categories. What does vary as these methods change is the relative importance of human health to ecosystem quality to resources for the processes. Human health is the largest factor for the individualist method while human health and resources become relatively more important for the hierarchist and egalitarian methods.

Scenario Analysis. One of the most useful aspects of LCA is the ability to make different assumptions to test various scenarios or the sensitivity of the models to data uncertainty. We have modeled two specific scenarios, which might be expected to change the results in a significant way.

First, ethanol is a solvent for both of the chemical processes and a significant contributor to the overall environmental impact. The method of its manufacturing varies depending on various economic and technical factors. In addition to production from corn fermentation, ethanol is also made by the hydration of ethylene. It might be expected that this latter ethylene would have higher environmental impacts since it is derived from a fossil resource rather than a biomass source like corn. This scenario was tested by selecting an LCI process based on ethylene hydration to replace corn ethanol. Second, the four baseline processes are all modeled from actual lab scale processes for the conversion of pulp to nanocellulose. While the results can help to make decisions at the lab scale, it would also be useful to gain insights into environmental impacts at the industrial scale based on the LCA analysis. To do so, we made the following modifications to the models to approximate expected differences at the industrial scale. To account for increased efficiencies due to industrial scale processing and equipment, we used only 8.3% of the direct electricity inputs (to drop the fibrillation energy to ~8000 kW h/ton, based on 2% consistency, single pass, rate of 5 mL/s, and working power 2.87 kW) from the baseline model corresponding to a process that is more energy efficient. In this industrial scenario, we also input and output only 20% of the ethanol and isopropanol solvent volumes for these processes by assuming that industrial scale processes will capture and recycle solvent at an 80% efficiency level. These assumptions provide less savings in electricity than the energy efficiency estimates in the Hohenthal et al.[40] nanocellulose LCI and Klemm et al. review;[9] however this shows relevant data achievable in a short-term industrial scenario based on the collected data in this study.

Figure 6 shows the cumulative energy demand for the baseline processes and two scenarios. For all cases, the

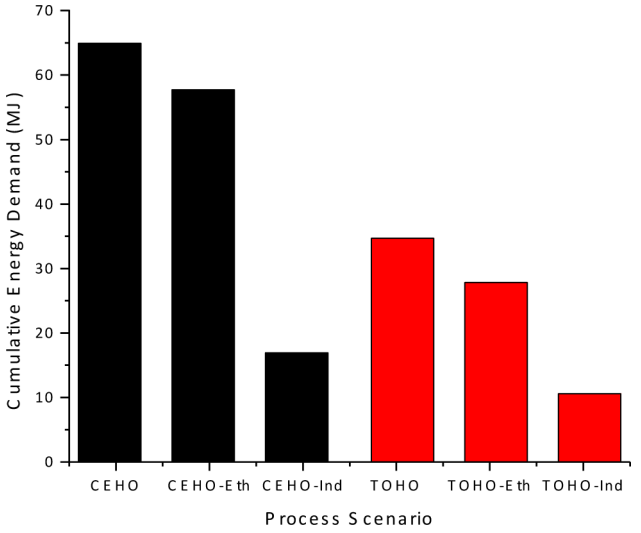


Figure 6. CED for nanocellulose baseline, ethylene-based ethanol, and estimated industrial scenarios.

ethylene-based ethanol has lower energy demand than the corn-based ethanol. This result is due to more energy demand for the extraction and processing of corn than many people would intuitively expect. This result is also supported by the EI99 comparison of ethanol sources shown in Figure 7 where CEHO is the baseline and CEHO_Ethylene is based on the ethylene-sourced ethanol. While the environmental impact for fossil fuels is lower for the corn-based ethanol, it does not overcome the higher impact for this form of ethanol for the land use impact category.

For the industrial scenario, one can also see in Figure 6 that energy demand for each case is lowest for this scenario due to the lower direct energy input and the smaller volume of solvent that is used and incinerated due to solvent recycling. While this is not a surprising result, once again the order of lowest to highest environmental impacts does not change for these scenarios compared to the baseline. Additionally, it is noted that while there has been an order of magnitude reduction in mechanical energy use, the overall energy consumption only is reduced by a factor of three because of the embodied energy within the chemical processes. These results highlight how LCA is useful to study the whole process relative to looking into a single factor (power consumed during fibrillation).

dx.doi.org/10.1021/sc4000225 | ACS Sustainable Chem. Eng. 2013, 1, 919−928

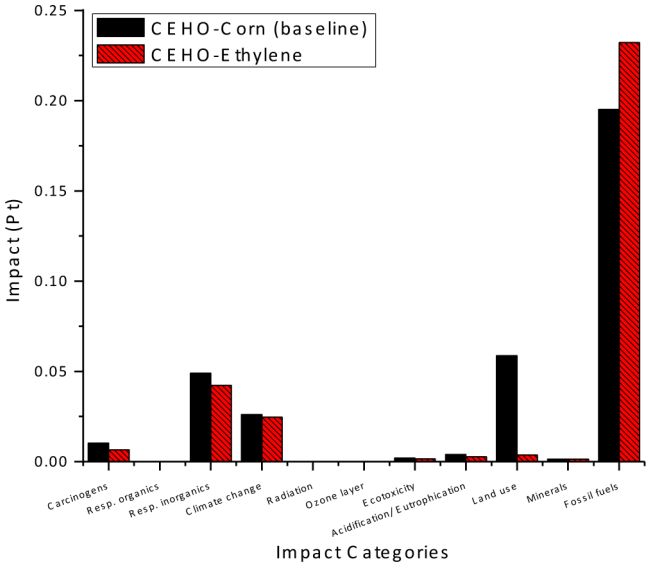


Figure 7. Baseline EI99 graph for baseline CEHO method with corn-based and ethanol-based ethanol scenario.

Nanocellulose Comparisons to Other Materials. In addition to relative comparisons of nanocellulose processes with each other, it is useful to compare this material to other nanomaterials to put the absolute metrics in context. First, it is useful to show the degree of impact for nanocellulose production relative to the kraft pulping process. Kraft pulp and MFC were compared to understand how much environmental impact increases for the nanocellulose fabrication compared to its precursor raw material. To model this, the kraft pulping process selected from the EcoInvent library in SimaPro was "Sulphate pulp, average, at regional storage/RER U", and this assumes that pulp is produced from an average technology European pulping facility. Sulfate pulp is the predominate fiber on the market and has a degree of polymerization greater than other high alpha cellulose content pulps. As the exponential growth of nanocellulose production is expected,[1,2] it is crucial to understand the potential environmental risks associated with this new material so that environmentally burdensome steps can be addressed proactively and to guide the emerging nanocellulose fabrication technologies toward the minimization of overall environmental impact.

The CED value for pulp is 2.5 MJ while the EI99 (H/H) score is 7.4 mPt. This compares with 34.7 MJ (10.6 MJ industrial scenario) and 164 mPt (45 mPt industrial scenario) for the lowest impact nanocellulose process (TOHO). These are factors of 10× (4× industrially) and 20× (6× industrially) of the energy and environmental impact for the nanocellulose compared to the raw pulp material, respectively. This estimate shows how quantifying the life cycle with LCA may shift the impression that surrounds some new technologies. To make further sense of these numbers, it should be noted that modern pulping technology is largely self-sustained from an energy and chemical recycling perspective;[50] hence the overall environmental burden is brought down substantially compared with other materials. Additionally, from the nanomaterials perspective, isolation of nanocellulose from native wood fiber's hierarchical structure is intrinsically an energy-intensive process.[21]

This LCA shows that direct energy consumption during nanocellulose processing accounts for significant fraction of environmental impact of its manufacturing. The processing of another popular nanomaterial, single-walled carbon nanotubes (SWNTs),[41,51,52] is generally considered to be very energy intensive. Hence the fabrication energy demand of nanocellulose was compared with SWNTs, to understand where nanocellulose stands relative to this material from an energy perspective. Ganter et al. reported electricity inputs for producing SWNT via laser vaporization in a lab setting at 114 000 kW h/kg.[52] Laser vaporization was reported having comparable energy consumption to other SWNT synthesis methods, but it is a promising approach to scale up and achieve substantial energy saving.[52] Scaling the direct electricity inputs for the lab scale nanocellulose TOHO chemical and mechanical processes produced 96 kW h/kg, less than 0.1% of the direct electricity input reported for processing SWNTs. This low energy consumption relative to SWNTs may provide nanocellulose with an environmental advantage in applications where the properties of both materials are acceptable. Moreover, to make these two nanomaterials more equivalent from a functional point of view, SWNTs must undergo additional processing (oxidation with acid mixtures) to achieve aqueous dispersible nanoparticles. One caveat regarding this comparison is that mass-based functional units are generally not appropriate in LCA. When considering a specific application, the relative amount of a nanomaterial required to achieve certain property enhancement is critical; i.e., if SWNTs require much less mass to achieve the same performance, then the energy consumption advantage of nanocellulose could be reduced proportionally.

Limitations. Like all LCAs, this assessment is a snapshot in time for the life cycle inventory which serves as the basis for the LCA model and impact assessment. As such, any changes in technology or processing conditions as well our understanding of the environmental impacts of the inputs and outputs (characterization factors) will lead to different results. This is an important consideration for researchers considering the results of this study as the differences between the processes studied in this case and future cases will increase and perhaps become more significant over time.

Because of this inherent limitation for LCA, the study has a number of factors, which should be discussed explicitly. The conclusions of this LCA are limited to the specific conditions in the laboratory setting and processes explained in detail. While many of the local lab conditions were based on measured primary data, most of the raw material processes were based on LCI data compiled at different times in different locations. As discussed, this study also does not accurately represent the industrial scale processing of nanocellulose, which will use different equipment and processes. Nonetheless, these results give insights into the specific inventory data necessary to complete an LCA at the commercial level. Moreover, reasonable estimates regarding potential environmental advantages of industrial processing such as more efficient equipment and recycling of solvents allowed scenarios to be tested.

The lab-scale comparison to SWNTs is also problematic for many of the reasons just outlined. However, on a relative basis, it is not unreasonable to assume that differences between nanocellulose and SWNTs will scale as both of these processes are transitioned to the industrial level.

Finally, it should be noted that current LCA impact methods, including the EI99 method used in this work, lack character-

ization factors for human and environmental toxicity effects due to nanomaterials. This study assumes no emissions of nanocellulose to the environment or interaction with humans. Even if these emissions were accurately modeled for this LCA scope or future cradle-to-cradles studies for nanocellulose containing products, more research to determine appropriate characterization factors for this material are necessary to accurately assess potential impacts.

CONCLUSIONS

The present work models a cradle-to-gate LCA for lab scale nanocellulose fabrication. Four fabrication routes (composed of two interchangeable chemical and mechanical processes) were evaluated using cumulative energy demand, global warming potential, and Eco-Indicator 99 impact assessment methods. This allowed quantification and comparison of the four methods across a range of environmental impacts. Scenarios to assess the sensitivity of the model to reasonable industrial scale process changes were also tested. The LCA results were also compared with the kraft pulping process and single-walled carbon nanotube (SWNT) fabrication.

The primary conclusions are as follows:

1. Sonication processes had more environmental impact that homogenization processes, and etherification had a greater impact than oxidation.
2. The TOHO process had the lowest environmental impact compared to the other processes for energy, global warming potential, and overall impact based on EcoIndicator 99.
3. Different assumptions for impact weighting, the source of ethanol, and estimations of industrial scale energy and solvent efficiency change the absolute values of the environmental impacts but not the relative impacts among the four processes studied. In this sense, the LCA methods were fairly insensitive to a wide range of assumptions when comparing processes, though individual processes did vary significantly under the different scenarios.
4. Comparing the laboratory data to the literature on energy consumption of fibrillation, it appears maximizing pulp concentration during scale-up will significantly impact mechanical energy demand. Additionally, this LCA study notes that inherent energy embodied within chemical modification (both etherification and oxidation) contributes greatly to nanocellulose's overall cumulative energy demand even if the mechanical energy is minimized. This finding implies that the oxidation or etherification reactions should be optimized as well.
5. Despite the lack of good inventory data for various aspects of this LCA, useful insights can be made regarding the overall impacts for these processes at the laboratory scale and likely be good predictors for some of the environmental issues at the industrial scale. Furthermore, based on the models developed from the laboratory procedures life cycle inventory data from pilot scale production will allow more accurate assessment of the potential environmental impacts for the scale-up of this nanomaterial for the industrial-scale processing of nanocellulose.

ASSOCIATED CONTENT

Supporting Information

PDF file containing nanocellulose inventory data for the four processes, network flow diagrams for the nanocellulose processing, and cost estimates for energy usage (USD). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: srenneck@vt.edu. Phone: 540-231-7100.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is sponsored by Virginia Tech Sustainable Nanotechnology Interdisciplinary Graduate Education Program (VTSuN IGEP), the Department of Sustainable Biomaterials at Virginia Tech. Additionally, this material is based upon work supported by the National Science Foundation under Grant No. 1236005. The authors also extend gratitude to Dr. P. Vikesland, Dr. A. Pruden, Paramjeet Pati, and Wei Zhang for their various contributions to this work.

REFERENCES

(1) Crotogino, R. *The Economic Impact of Nanocellulose*; Arbora Nano: Washington D.C., March 27−28, 2012.
(2) TAPPI. *International Nanocellulose Standards—The Need and Purpose of Standards for Nanocellulosic Materials*; TAPPI: Norcross, GA, June 9, 2011.
(3) US Environmental Protection Agency. *Defining Life Cycle Assessment*. http://www.gdrc.org/uem/lca/lca-define.html (accessed Jan 2013).
(4) *Environmental management—Life cycle assessment—Principles and framework*; ISO: Geneva, Switzerland, 2006; ISO 14040:2006.
(5) Curran, M. A. *Life Cycle Assessment: Principles and Practice*; U.S. Environmental Protection Agency: Cincinnati, 2006; p 88.
(6) Guinee, J. B.; Heijungs, R. In *Life cycle assessment*; John Wiley & Sons, Inc.: New York, 2005; pp 805−831.
(7) Righi, S.; Morfino, A.; Galletti, P.; Samori, C.; Tugnoli, A.; Stramigioli, C., Comparative cradle-to-gate life cycle assessments of cellulose dissolution with 1-butyl-3-methylimidazolium chloride and N-methyl-morpholine-N-oxide. *Green Chem* **2011**, *13* (2).
(8) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev* **2011**, *40* (7), 3941−3994.
(9) Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris, A. Nanocelluloses: A New Family of Nature-Based Materials. *Angew. Chem. Int. Ed.* **2011**, *50* (24), 5438−5466.
(10) Isogai, A.; Saito, T.; Fukuzumi, H. TEMPO-oxidized cellulose nanofibers. *Nanoscale* **2011**, *3* (1), 71−85.
(11) Fernandes, A. N.; Thomas, L. H.; Altaner, C. M.; Callow, P.; Forsyth, V. T.; Apperley, D. C.; Kennedy, C. J.; Jarvis, M. C. Nanostructure of cellulose microfibrils in spruce wood. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, E1195−E1203.
(12) Eichhorn, S. J. Cellulose nanowhiskers: promising materials for advanced applications. *Soft Matter* **2011**, *7*, 303−315.
(13) Klemm, D.; Schumann, D.; Kramer, F.; Hessler, N.; Hornung, M.; Schmauder, H. P.; Marsch, S., Nanocelluloses as innovative polymers in research and application. In *Polysaccharides II*; Springer-Verlag Berlin: Berlin, 2006; Vol. *205*, pp 49−96.
(14) Li, Z.; Renneckar, S.; Barone, J. Nanocomposites prepared by in situ enzymatic polymerization of phenol with TEMPO-oxidized nanocellulose. *Cellulose* **2010**, *17* (1), 57−68.
(15) Johnson, R. K.; Zink-Sharp, A.; Renneckar, S. H.; Glasser, W. G. A new bio-based nanocomposite: fibrillated TEMPO-oxidized

celluloses in hydroxypropylcellulose matrix. *Cellulose* **2009**, *16* (2), 227−238.
(16) Wagberg, L.; Decher, G.; Norgren, M.; Lindstrom, T.; Ankerfors, M.; Axnas, K. The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir* **2008**, *24* (3), 784−95.
(17) Iwamoto, S.; Nakagaito, A. N.; Yano, H.; Nogi, M. Optically transparent composites reinforced with plant fiber-based nanofibers. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *81*, 1109−1112.
(18) Nakagaito, A. N.; Yano, H. Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *80*, 155−159.
(19) Fukuzumi, H.; Saito, T.; Iwata, T.; Kumamoto, Y.; Isogai, A. , Transparent and High Gas Barrier Films of Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation. *Biomacromolecules* **2008**, *10* (1), 162−165.
(20) Hentze, H.-P. In *From Nanocellulose Science towards Applications*;Technical Research Center of Finland: Helsinki, 2010.
(21) Atalla, R. H.; Brady, J. W.; Matthews, J. F.; Ding, S.-Y.; Himmel, M. E. Structures of Plant Cell Wall Celluloses. In *Biomass recalcitrance: deconstructing the plant cell wall for bioenergy*; Himmel, M. E., Ed.; Blackwell Pub.: Oxford, 2008; Vol. *xviii*.
(22) Ross, P.; Mayer, R.; Benziman, M. Cellulose biosynthesis and function in bacteria. *Microbiol. Mol. Biol. Rev.* **1991**, *55* (1), 35−58.
(23) Spence, K. L.; Venditti, R. A.; Rojas, O. J.; Habibi, Y.; Pawlak, J. J. A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods. *Cellulose* **2011**, *18* (4), 1097−1111.
(24) Dong, S.; Roman, M. Fluorescently Labeled Cellulose Nanocrystals for Bioimaging Applications. *J. Am. Chem. Soc.* **2007**, *129* (45), 13810−13811.
(25) Beck-Candanedo, S.; Roman, M.; Gray, D. G. Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions. *Biomacromolecules* **2005**, *6* (2), 1048−1054.
(26) Wikipedia.org Nata de coco. http://en.wikipedia.org/wiki/Nata_de_coco (accessed July 2012).
(27) Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1983**, *37*, 815−827.
(28) Wuhrmann, K.; Heuberger, A.; Muhlethaler, K. Electron-microscopic investigations of cellulose fibers after supersonic treatment. *Experientia* **1946**, *2*, 105−7.
(29) Faria Tischer, P. C. S.; Sierakowski, M. R.; Westfahl, H., Jr.; Tischer, C. A. Nanostructural Reorganization of Bacterial Cellulose by Ultrasonic Treatment. *Biomacromolecules* **2010**, *11* (5), 1217−1224.
(30) Li, Q.; Renneckar, S. Molecularly thin nanoparticles from cellulose: isolation of sub-microfibrillar structures. *Cellulose* **2009**, *16* (6), 1025−1032.
(31) Elazzouzi-Hafraoui, S.; Nishiyama, Y.; Putaux, J. L.; Heux, L.; Dubreuil, F.; Rochas, C. The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacromolecules* **2008**, *9* (1), 57−65.
(32) Saito, T.; Nishiyama, Y.; Putaux, J. L.; Vignon, M.; Isogai, A. Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* **2006**, *7* (6), 1687−1691.
(33) Cheng, Q.; Wang, S.; Han, Q. Novel process for isolating fibrils from cellulose fibers by high-intensity ultrasonication. II. Fibril characterization. *J. Appl. Polym. Sci.* **2009**, *115* (5), 2756−2762.
(34) Eyholzer, C.; Bordeanu, N.; Lopez-Suevos, F.; Rentsch, D.; Zimmermann, T.; Oksman, K. Preparation and characterization of water-redispersible nanofibrillated cellulose in powder form. *Cellulose* **2010**, *17* (1), 19−30.
(35) Bondeson, D.; Mathew, A.; Oksman, K. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose* **2006**, *13* (2), 171−180.
(36) Pääkkö, M.; Ankerfors, M.; Kosonen, H.; Nykänen, A.; Ahola, S.; Österberg, M.; Ruokolainen, J.; Laine, J.; Larsson, P. T.; Ikkala, O.; Lindström, T. Enzymatic Hydrolysis Combined with Mechanical Shearing and High-Pressure Homogenization for Nanoscale Cellulose Fibrils and Strong Gels. *Biomacromolecules* **2007**, *8* (6), 1934−1941.
(37) Eichhorn, S. J.; Dufresne, A.; Aranguren, M.; Marcovich, N. E.; Capadona, J. R.; Rowan, S. J.; Weder, C.; Thielemans, W.; Roman, M.; Renneckar, S.; Gindl, W.; Veigel, S.; Keckes, J.; Yano, H.; Abe, K.; Nogi, M.; Nakagaito, A. N.; Mangalam, A.; Simonsen, J.; Benight, A. S.; Bismarck, A.; Berglund, L. A.; Peijs, T. Review: current international research into cellulose nanofibres and nanocomposites. *J. Mater. Sci.* **2010**, *45* (1), 1−33.
(38) Denooy, A. E. J.; Besemer, A. C.; Vanbekkum, H. Selective oxidation of primary alcohols mediated by nitroxyl radical in aqueous-solution- kinetics and mechanism. *Tetrahedron* **1995**, *51* (29), 8023−8032.
(39) Li, Q.; Renneckar, S. Supramolecular Structure Characterization of Molecularly Thin Cellulose I Nanoparticles. *Biomacromolecules* **2011**, *12* (3), 650−659.
(40) Hohenthal, C.; Ovaskainen, M.; Bussini, D.; Sadocco, P.; Pajula, T.; Lehtinen, H.; Kautto, J.; Salmenkivi, K. *Final Assessment of Nano Enhanced New Products*; VTT Technical Research Centre of Finland, 2012; p 56.
(41) Wender, B. A.; Seager, T. P. Towards prospective life cycle assessment: Single wall carbon nanotubes for lithium-ion batteries, *2011 IEEE International Symposium on Sustainable Systems and Technology (ISSST)*, Chicago, IL, May 16−18, 2011; pp 1−4.
(42) Goedkoop, M.; Spriensma, R. *The Eco-indicator 99 A Damage Oriented Method for Life Cycle Impact Assessment*; PRé Consultants: June 22, 2001.
(43) Wikipedia.org Sodium Chloride. http://en.wikipedia.org/wiki/Sodium_chloride (accessed July 2012).
(44) Wikipedia.org Sodium Bromide. http://en.wikipedia.org/wiki/Sodium_bromide (accessed July 2012).
(45) Althaus, H.-J.; Bauer, C.; Doka, G.; Dones, R.; Hischier, R.; Hellweg, S.; Humbert, S.; Köllner, T.; Loerincik, Y.; Margni, M.; Nemecek, T. *Implementation of Life Cycle Impact Assessment Methods*; Swiss Centre for Life Cycle Inventories: St-Gallen, Switzerland, 2007; p 151.
(46) Huijbregts, M. A.; Hellweg, S.; Frischknecht, R.; Hendriks, H. W.; Hungerbühler, K.; Hendriks, A. J. Cumulative energy demand as predictor for the environmental burden of commodity production. *Environ. Sci. Technol.* **2010**, *44* (6), 2189−2196.
(47) IPCC. *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Intergovernmental Panel on Climate Change: Cambridge, United Kingdom, 2007; p 996.
(48) Audenaert, A.; De Cleyn, S. H.; Buyle, M. LCA of low-energy flats using the Eco-indicator 99 method: Impact of insulation materials. *Energy Buildings* **2012**, *47* (0), 68−73.
(49) Dreyer, L.; Niemann, A.; Hauschild, M. Comparison of Three Different LCIA Methods: EDIP97, CML2001, and Eco-indicator 99. *Int. J. Life Cycle Assess.* **2003**, *8* (4), 191−200.
(50) Zhi Fu, G.; Chan, A.; Minns, D. Preliminary Assessment of the Environmental Benefits of Enzyme Bleaching for Pulp and Paper Making (7 pp). *Int. J. Life. Cycle Assess.* **2005**, *10* (2), 136−142.
(51) Peralta-Videa, J. R.; Zhao, L.; Lopez-Moreno, M. L.; de la Rosa, G.; Hong, J.; Gardea-Torresdey, J. L. Nanomaterials and the environment: a review for the biennium 2008−2010. *J. Hazard. Mater.* **2011**, *186* (1), 1−15.
(52) Ganter, M. J.; Seager, T. P.; Schauerman, C. M.; Landi, B. J.; Raffaelle, R. P. A life-cycle energy analysis of single wall carbon nanotubes produced through laser vaporization. *ISSST '09. IEEE International Symposium on Sustainable Systems and Technology*, Phoenix, AZ, May 18−20, 2009; pp 1−4.