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Life cycle assessment of cellulose nanowhiskers

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ABSTRACT

Cellulose nanowhiskers refer to elongated, single crystalline, rod-like particles that have at least 1 nm-size dimension. Vegetal fibers are an important source of cellulose for the extraction of nanowhiskers that can be used to reinforce the mechanical properties of different polymers. The present study contributes to the environmental performance of cellulose nanowhiskers production processes at their development stage. Thus, particular environmental aspects and related impacts of two cellulose nanowhiskers product systems are evaluated: nanowhiskers extracted from unripe coconut fibers (EUC system) and from white cotton fibers (EC system). The product systems encompassed fiber, electricity, and chemical production processes. All aspects were measured considering the production of 1 g of nanowhiskers. Life cycle inventory analysis was performed while considering the following environmental aspects: energy, water and emissions present in liquid effluents (chemical oxygen demand (COD), biological oxygen demand (BOD), total nitrogen, nitrate, total phosphorus, phenols, furfural, and hydroxymethylfurfural (HMF)). Life cycle impact was also assessed for climate change, water depletion, eutrophication, and human toxicity impact categories. The comparison between the EUC and EC systems showed that nanowhiskers produced in the EC system required less energy and water, emitted less pollutants, and contributed less to climate change, human toxicity, and eutrophication than those produced in the EUC system. Further research to improve the environmental performance of these systems – before scaling up the results from the laboratory to industry – shall focus on improving yield efficiency, reducing energy and water use during the extraction of nanowhiskers, and recovering substances from effluents possessing market value.

1. Introduction

Innovations in the field of nanotechnology have been steadily increasing in recent years. According to the Woodrow Wilson International Center for Scholars (2009), over 1,000 nanotechnology-enabled products were available to consumers in 2009, and over 2,000 products are expected to be available by 2015. This development is primarily explained by the promising properties of nanoparticles (which have at least one dimension in the range of 0.1–100 nm) and nanotechnology-enabled products (nanoproducts) that incorporate such particles. Nanoparticles and nanoproducts are expected to benefit many sectors. Features of nanoparticles can foster renewable energy, enable the detection capacity of sensors, improve wastewater treatment, scale material strength, and reduce raw material use, among many other possibilities (Hannah and Thompson, 2008).

In the food sector, nanoparticles have been used mostly as fillers in polymer packaging (FAO and WHO, 2010). In food packing, nanoparticles may improve the mechanical and barrier properties of polymers, reduce material weight, inhibit microbial activity, and detect leaks, temperature variations, and food deterioration. Cellulose nanowhiskers, microcrystalline cellulose, nanoclay, starch nanocrystals, chitin whiskers, nanosilica, carbon nanofibers, and carbon nanotubes are examples of nanoparticles that can improve the mechanical properties of different kinds of polymers (Samir et al., 2005; Joshi, 2008; Khanna et al., 2008; Azeredo, 2009; FAO and WHO, 2010).

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Despite outstanding developments in nanotechnology, environmental issues in this area remain little understood. International governmental organizations and scientists worldwide have called for research on the toxicological effects of nanoparticles and nanoproducts (Reijnders, 2006; Rickerby and Morrinson, 2007; Boccuni et al., 2008; FAO and WHO, 2010; Ellenbecker and Tsai, 2011) and for the assessment of life cycle environmental impacts (Karn and Aguar, 2006; Bauer et al., 2008; von Gleich et al., 2008). Scientific discussions about the benefits and environmental risks of nanotechnologies were the subject of a special issue of this journal: Sustainable Nanotechnology Development (Helland and Kastenholz, 2008).

Few studies have been published concerning the life cycle assessment (LCA) of nanoparticles that could be used as fillers in polymers. None of these studies concerns cellulose nanowhiskers. Khanna et al. (2008) presented a life cycle impact assessment of carbon nanofibers that addressed a range of feedstock materials (such as methane, ethylene, and benzene), energy, and other inputs required for their production. Joshi (2008) performed a life cycle inventory analysis of organically modified montmorillonite clay (nanoclays) that accounted for energy demands and emissions into air and water over the life cycle of this product. Inputs and outputs of the nanoclay inventory were also compared to pristine biopolymers (PLA, PHA, and PHB), glass fiber, and China-reed fiber. Singh et al. (2008) performed a comparative life cycle impact assessment of two catalytic, chemical vapor deposition processes (the high-pressure carbon monoxide disproportionation in a plug-flow reactor (CNT-PFR) and the cobaltmolybdenum fluidized bed catalytic reactor (CNT-FBR)) used in the production of carbon nanotubes that showed resource consumption and emissions of these processes. Kushnir and Sandén (2008) measured the energy requirements for the synthesis of nanotubes and analyzed numerous production processes.

The development of new cellulose nanowhiskers extracting processes fosters discussions related to the environmental impacts of these processes and the actions that may reduce these impacts. This research assesses the life cycle aspects and impacts of two cellulose nanowhiskers obtained from unripe coconut and white cotton fibers. Two different product systems are compared and defined by considering the processes used to extract nanowhiskers from each fiber: the product systems that emerge when unripe coconut fiber is used (EUC system) and when white cotton fiber is used (EC system). Opportunities to reduce impacts along these product systems are discussed.

This study contributes to the scientific debate in nanotechnology regarding important environmental aspects and impacts of extracting cellulose nanowhiskers. This research also contributes to future studies intending to improve the product's environmental performance while still at the laboratorial stage and supports the continuous work of research teams toward the development of sustainable innovations.

The discussion considers the main characteristics of cellulose nanowhiskers and then analyzes the life cycle impact of these nanoparticles. The chemical composition of fibers, the technological processes, and the properties of the obtained cellulose nanowhiskers are discussed. The inventory and impact assessment of the EC and EUC systems are compared while considering uncertainties and selected categories that are especially relevant in the study of cellulose nanoparticles, such as human toxicity, climate change, water depletion, and eutrophication. The obtained results are also compared to former studies of nanoparticles that may have similar function in the mechanical properties of composites.

2. Cellulose nanowhiskers

Cellulose is the most abundant polymer available on earth. Cellulose is found in both plants, such as wood, hemp, cotton, and coconut fibers, and non-plant sources, such as forms produced by bacteria and found in tunicates (Eichhorn et al., 2010). Cellulose is a carbohydrate formed by crystalline and disordered amorphous domains. Cellulose chains are organized into micro fibrils (Battista, 1975) surrounded by a matrix of lignin, extractives, inorganics, and hemicellulose in plant cell walls (Fengel and Wegener, 2003). Thus, lignin, extractives, inorganics, and hemicellulose must be extracted and cellulose chains deconstructed in order to extract cellulose nanowhiskers from plant fibers.

According to Eichhorn et al. (2010), the term nanowhisker refers to elongated, single crystalline, rod-like particles that have at least 1 nm-size dimension. This nanoparticle can be obtained from various sources of natural fibers, such as cotton (Teixeira et al., 2010a), sugar cane bagasse (Teixeira et al., 2010b), and unripe coconut husks (Rosa et al., 2010). The main benefits linked to this nanoparticle include exceptional mechanical properties (high specific strength and modulus), environmental benefits, and low cost (Orts et al., 2005; Medeiros et al., 2008a, 2008b).

Nanowhiskers can be obtained by submitting a natural fiber to chemical hydrolysis or combining high mechanical shearing forces with enzymatic hydrolysis. Currently, chemical hydrolysis is the most researched route (Eichhorn et al., 2010; Rosa et al., 2010; Teixeira et al., 2010a, 2010b).

Rosa et al. (2010) defined the technical process to obtain cellulose nanowhiskers from unripe coconut, and Teixeira et al. (2010a) defined the technical process to obtain cellulose nanowhiskers from cotton fibers at the laboratorial stage in the Brazilian Agricultural Research Corporation (Embrapa). The cellulose nanowhiskers obtained from these processes are not commercial; their properties and further use in films are still being investigated.

The cellulose, lignin, and hemicellulose content of these fibers are quite different, as presented in Table 1. Cotton fibers have higher cellulose content than unripe coconut fibers, which are rich in lignin and hemicellulose. Unripe coconut fiber is a relatively new material extracted from the unripe coconut husks, an undesirable waste of coastal cities in Brazil that poses serious problems when disposed in landfills (Rosa et al., 2009). On the other hand, cotton fibers already exhibit a range of uses in the medical and textile sectors.

Suspensions of nanowhiskers were obtained by the acid hydrolysis of unripe coconut and cotton fibers. The dimensions, aspect ratio, crystallinity index (C_I), and initial temperature of thermal degradation for nanowhiskers from unripe coconut and cotton fibers are presented in Table 2. Cellulose nanowhiskers from coconut fibers have diameters as low as 4 nm and an aspect ratio of up to 53, higher than when compared to values obtained from cotton fibers. As a result, a better mechanical performance is expected. Apart from this, the presence of remaining lignin in nanowhiskers from coconut fiber can represent an advantage in improving compatibility with hydrophobic matrixes (Alexy et al., 2008). On the other hand, nanowhiskers from cotton fibers have higher thermal stability when compared to nanowhiskers from coconut fibers, as well as higher crystallinity, due to the high cellulose content of the raw material.

Table 1
Fractions of main constituents of white cotton and unripe coconut fibers.

Fiber	Hemicellulose (%)	Cellulose (%)	Lignin (%)
White cotton[a]	0.5	97.7	0.4
Unripe coconut[b]	29.25	28.23	37.2

Source
[a] Teixeira et al. (2010a).
[b] Corradini et al. (2009).

Table 2
Dimensions (diameter, length), aspect ratio, crystallinity index (C_I), and initial temperature of thermal degradation (Tid) for nanowhiskers from unripe coconut and cotton fibers.

Type	Diameter (D, nm) [a]	Length (L, nm) [a]	Aspect ratio (L/D) [a]	C_I (%)	Tid (°C)
White cotton[b]	14 ± 4	135 ± 50	11 ± 7	91	220
Unripe coconut[c]	5.5 ± 1.5	194 ± 70	39 ± 14	66	170

Source
[a] Values expressed as means ± standard deviations.
[b] Teixeira et al. (2010).
[c] Rosa et al. (2010).

3. Life cycle assessment

This study analyzes two product systems used to obtain cellulose nanowhiskers: ECU (nanowhiskers extraction from unripe coconut fibers) and EC (extraction from white cotton fibers). LCA was the method chosen to evaluate the environmental performances of these systems. Although information regarding the health and safety of nanoparticles is scarce (Boccuni et al., 2008; Demou et al., 2011) and toxicity of these materials is not present in commonly available life cycle inventory databases (Bauer et al., 2008), LCA is widely recognized as a good tool to identify environmental bottlenecks of processes and products at their research and development stage as well as opportunities to further improve their efficiency (Fleischer and Grunwald, 2008; von Gleich et al., 2008; Ellenbecker and Tsai, 2011).

The environmental aspects analyzed in each system studied included energy, water, and emissions present in liquid effluents, related to chemical oxygen demand (COD), biological oxygen demand (BOD), total nitrogen, nitrate, total phosphorus, phenols, furfural, and hydroxymethylfurfural (HMF). These water emissions were selected because they are typical emissions resulting from pulp processing under acidic conditions (Fengel and Wegener, 2003), a process similar to the ones used to extract cellulose nanowhiskers. Because carbon dioxide is not expected to be released under the temperatures that fibers are subject to (Fengel and Wegener, 2003) during cellulose nanowhiskers extraction (item 3.1), no measurements were made to quantify this substance. This study did not consider other substances that may be released to air or water, suc as the emissions of nitrogen and sulfur oxides into the air and sulfates and sulfuric acid into water. This supposition was based on the reagents used in the nanowhiskers extraction processes (e.g., nitric acid and sulfuric acid), although the literature regarding the chemistry of cellulose does not mention the presence of these reagents in effluents from related processes (Fengel and Wegener, 2003). In order to really determine their relevance, it is necessary to conduct research that makes measurements of these compounds on samples of effluents.

The environmental impact categories considered include climate change, water depletion, eutrophication, and human toxicity. They are evaluated using the ReCiPe method, hierarchist version (Goedkoop et al., 2009) that considers midpoint results. This method uses models to calculate characterization factors, considering the European environmental conditions.

In the ReCiPe method, climate change takes into account the radioactive forcing of the substances and their residence time in the atmosphere, according to the Intergovernmental Panel on Climate Change (IPCC). The results are expressed in CO_2-equivalents. Water depletion measures the volume of water (by cubic meters) used while considering water categories that contribute to water shortages. The eutrophication category encompasses freshwater eutrophication caused by phosphorous emissions (expressed as kilograms of phosphorus equivalent), and marine eutrophication caused by nitrogen emissions (expressed as kilograms of nitrogen equivalent). Human toxicity accounts for the human toxicity potential of substances, taking 1,4-dichlorobenzene as a reference substance in the midpoint calculations (expressed as kilograms of 1.4 DB equivalent). Currently, the toxicity potential of nanoparticles is not considered by ReCiPe or other life cycle impact assessment methods. Toxicological studies of cellulose nanowhiskers are being performed as part of Embrapa's Nanotechnology Network Applied to Agribusiness.

The ReCiPe method uses the most updated human toxicity model, USES (the Uniform System for the Evaluation of Substances), and addresses impacts on water depletion and marine and freshwater eutrophication (Goedkoop et al., 2009). Other life cycle impact methods link COD to marine (e.g. Traci (Bare et al., 2003)) or freshwater eutrophication (e.g. Impact 2002+ (Jolliet et al., 2003)), but do not present characterization factors to both midpoint categories nor consider the water depletion category. Impact 2002+ considers furfural emissions to water in the assessment of human toxicity, but does not consider the impacts of phenols and HMF. For these reasons, ReCiPe was used to assess the mentioned impact categories.

Uncertainty of the results from the inventory and environmental impact analysis were carried out using the Monte Carlo method by considering 1,000 cycles and a confidence interval of 95 percent (Goedkoop et al., 2008). The next section presents information about the cellulose nanowhiskers extraction processes, the systems boundaries, the functional unit used, and data collection.

3.1. Nanowhiskers extraction processes

As previously mentioned, cellulose nanowhiskers in this study were obtained through chemical acid hydrolysis. However, differences in the extraction process depending on the source of cellulose used should be noted.

The extraction Process 1, followed when unripe coconut fiber was used, was performed according to Rosa et al. (2010). The extraction Process 2, which was followed when white cotton was used, followed the procedure established by Teixeira et al. (2010a). Both processes require chopping the fibers into smaller pieces, which is followed by their hydrolysis with sulfuric acid. However, different hydrolysis conditions regarding temperature and mass of sulfuric acid were used to break down the amorphous domains present in the cellulose chains of these fibers.

Because of the high lignin content of the unripe coconut fiber, a pre-treatment was also necessary to remove the lignin fraction in Process 1. The pre-treatment involves washing fibers with water and sodium hydroxide and then bleaching the washed fibers using sodium chlorite, nitric acid, and acetic acid (Rosa et al., 2010).

3.1.1. Extraction of nanowhiskers from unripe coconut fiber

The extraction of nanowhiskers was performed following five steps (Rosa et al., 2010):

- Chopping: fibers were chopped in a Wiley mill and sieved through a 35-mesh sieve.
- Washing: fibers (100 g) were dispersed in tap water (500 mL) for 10 min in a Croydon Laboratory Blender at full speed. This suspension was stirred for 2 h at 50 °C and filtered in order to remove soluble extractives in the water. This procedure was repeated once more. The residue was dispersed in 500 mL of a 2% (m/v) NaOH solution and the suspension was stirred for 2 h at 80 °C, filtered, and then washed with water. After washing, the alkaline treatment was repeated once again, and the fibers were dried at room temperature.
- Bleaching: because lignin hinders fiber separation by acid hydrolysis, partial delignification (bleaching) was performed in

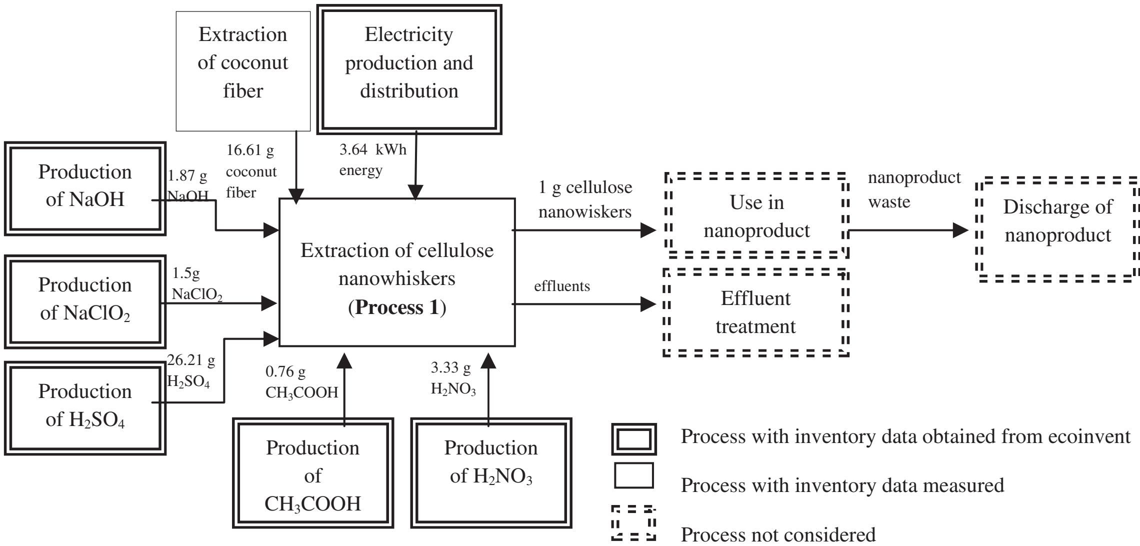

Fig. 1. EUC system boundary (nanowhiskers from unripe coconut fiber).

order to facilitate further whisker extraction. First, 5 g of dried pretreated fibers were heated between 60 and 70 °C in 150 mL of water containing 1.5 g $NaClO_2$ and 8–10 drops of glacial acetic acid. The mixture was stirred at frequent intervals for 1 h, then cooled in an ice bath, filtered, and washed with cold water until the pH reached 6–7. The bleached pulp was treated with a 0.05 N nitric acid solution for 1 h at 70 °C, sieved in a 120 lm mesh size sieve, and washed thoroughly with water.

- Hydrolysis: the bleached fibers were treated in a concentrated sulfuric acid solution (64% w/w sulfuric acid in water) at 45 °C for 120 min, under constant stirring. After treatment, the hydrolyzed cellulose samples were concentrated four times, separating the crystals from the solution by centrifugation (10,000 rpm, 10 min).
- Dialysis: The resultant precipitate kept in a cellulose membrane was continuously dialyzed against water until constant pH reached 6–7.

3.1.2. *Extraction of nanowhiskers from cotton fibers*

Nanowhiskers from white cotton fibers were obtained following three steps (Teixeira et al., 2010a):

- Chopping: initially cotton fibers were chopped in a Solab mill and sieved through a 35-mesh sieve.
- Hydrolysis: about 5.0 g of fibers were dispersed in a concentrated sulfuric acid solution (60% w/w sulfuric acid in water) at 45 °C and stirred vigorously for 75 min. After that, 500 mL of cold distilled water was added to stop the reaction. The sulfuric acid was partially removed from the resulting suspension by centrifugation at 10,000 rpm for 10 min.
- Dialysis: the solution containing nanowhiskers kept in a cellulose membrane was dialyzed against tap water until the pH reached 6–7.

3.2. *Systems boundaries*

Because two processes were used to extract cellulose nanowhiskers from two natural fibers, two different product systems are under study: EUC (extraction process using unripe coconut fiber) and EC (extraction process from cotton fiber). The boundaries of the EUC system, shown in Fig. 1, encompass the production of unripe coconut fiber, nanowhiskers, electricity, and chemical reagents (sodium hydroxide, acetic acid, nitric acid, sodium chlorite, and sulfuric acid) necessary to obtain nanowhiskers from this fiber. The agricultural production of unripe coconut was not considered in this study because unripe coconut fiber is obtained from coconut husks, a material still considered a residue with no market value. Transportation of coconut husks to fiber production units was disregarded because many of these units are installed in proximity to companies that extract coconut water.

The system boundary for EC, presented in Fig. 2, encompasses the agricultural production of cotton and the production of nanowhiskers, electricity, and chemical reagents (sulfuric acid) necessary to obtain nanowhiskers from cotton fiber. The total amount of resources used in EC and EUC are also presented in Figs. 1 and 2.

The transportation of materials (such as chemicals and fibers) was not included in EC and EUC because the cellulose nanowhiskers extraction processes are still at the laboratorial stage and the locations of the production units have not yet been determined.

As soon as the processes that incorporate cellulose nanowhiskers into composites are technically defined, this system boundary shall be expanded to encompass the use and end-of-life phases of cellulose nanowhiskers. Such system expansion will also require a functional unit that will be related to the properties of the new composites.

3.3. *Functional unit*

The function of the studied processes was the extraction of nanowhiskers. The functional unit adopted served to extract 1 g of cellulose nanowhiskers. Although cellulose nanowhiskers were diluted in a solution at the end of the extraction process, this solution was dried in order to determine the mass of cellulose nanowhiskers obtained in each process studied.

3.4. *Data collection*

Data from the extraction of unripe coconut fiber and cellulose nanowhiskers was measured on site, while data related to production and distribution of electricity and production of reagents was obtained from the ecoinvent v2 database, as shown in Figs. 1 and 2 and described in Annex A. Consumption of resources usage and emissions from the extraction of unripe coconut fiber

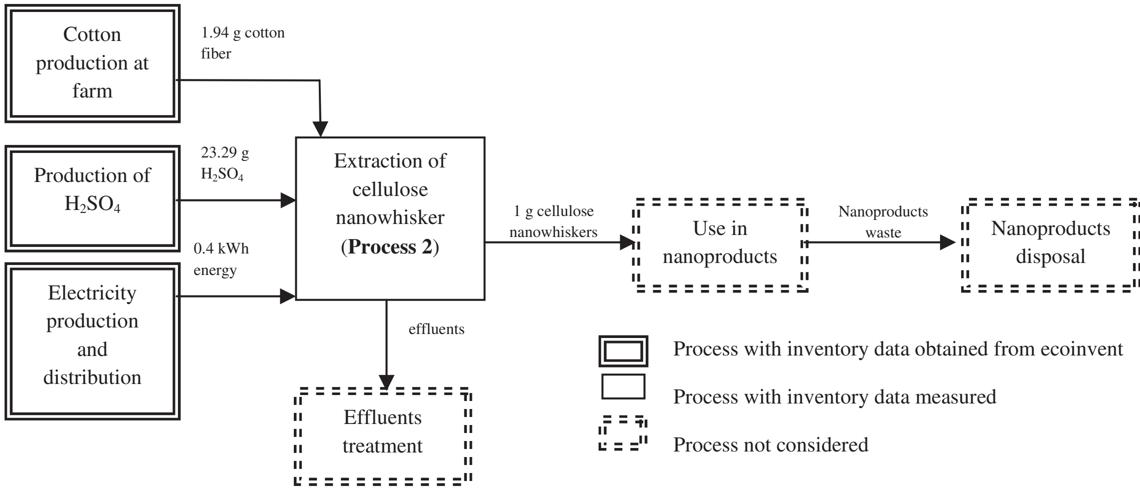

Fig. 2. EC system boundary (nanowhiskers from cotton fiber).

were measured in two production units located in the State of Ceará (Figueirêdo, 2008). Because the extraction process of cellulose nanowhiskers from unripe coconut fiber and cotton fiber are still at the laboratory stage, data from these processes were measured at Embrapa laboratorial facilities. The concentrations of COD, BOD, total nitrogen, nitrate, total phosphorus, and phenols in liquid effluents were determined according to APHA et al. (2006) and Silva and Oliveira (2001).

The procedure used to determine the concentrations of furfural and HMF was based on Rocha et al. (2009) by applying the following conditions: column Agilent Zorbax SB C-18 at 25 °C; column maintained by ultraviolet/visible detector Varian to 276 nm, using acetonitrile/water (2:8) with one percent acetic acid as effluent in flux of 0.7 mL min^{-1}. The sample volume injected was 20 L. Samples were previously filtrated using cellulose acetate membrane ME25 with 0.45 L and D13 mm.

4. Results

4.1. Life cycle inventory

The life cycle inventory of EUC and EC systems regarding water, energy, and effluent loads are presented in Table 3. The comparison of these processes shows that when unripe coconut fibers were used, water and energy consumption increased, as well as the loads of most of the substances studied.

These results can be explained partially by the cellulose content of the natural fibers and by the low yield of processes 1 and 2. Because the unripe coconut fiber has lower cellulose (28 percent of cellulose) content than cotton fiber (97 percent of cellulose), but higher lignin and hemicellulose (Table 1), a great effort was made to remove these undesirable fractions from this material, leading to higher resource consumption and polluting loads.

On the other hand, only six percent of the unripe coconut fibers were converted to nanowhiskers. The low yield of this fiber came primarily from losses during the pre-treatment steps. A significant part of the initial mass of the coconut fibers (77 percent) was lost during the chopping, washing, and bleaching steps. The chopping of coconut fibers, when only physical modification of this fiber occurred, accounted for 57 percent of the total fiber loss in the pre-treatment steps. As 26 percent of the mass of coconut fiber used in the hydrolysis step was converted to nanowhiskers, this step can be improved because this mass content was primarily cellulose.

Process 2 yield was higher (52 percent) than Process 1, but still low when compared to the cellulose content of cotton fibers (97 percent). In this case, low fiber loss (9 percent) occurred in the chopping step, and major loss occurred during the hydrolysis step.

4.1.1. Energy

The energy demanded by the EUC system was significantly higher than the energy necessary for EC (Table 3). This energy demand, in both systems, was mostly derived from the processes responsible for nanowhisker extraction (Processes 1 and 2), as noted in Figs. 3 and 4. The energy necessary for the production of chemicals is insignificant when compared to the energy demanded by Processes 1 and 2. Energy in Processes 1 and 2 were related to the electricity required to chop fibers and warm up chemical solutions.

If the energy demanded to make 1 g of cellulose nanowhiskers in the EUC system is compared to the energy required to make the same quantity of carbon nanotubes, carbon nanofibers, or nanoclays, then cellulose nanowhiskers are also energy intensive, especially those produced in the EUC system. As much as 9,635 kJ are required to produce 1 g of carbon nanotube using laser ablation (Kushnir and Sandén, 2008), between 10,925 and 20,000 kJ are needed to produce 1 g of carbon nanofiber using methane as feedstock (Khanna et al., 2008), and 40.07 kJ are necessary to produce 1 g of nanoclay (Joshi, 2008). According to Sengül et al. (2008), processes used in the manufacturing of nanoparticles are usually energy intensive.

4.1.2. Water

The total volume of water required by the EUC system is significantly higher than that required by EC (Table 3). Most of the water volume required by EUC (99.57 percent) and by EC (96.16 percent) is used in turbines at hydropower plants for the production of the energy demanded by these processes. Thus, electricity production and distribution is the main process responsible for water use in both systems (Figs. 3 and 4).

No information regarding the total water use in the life cycle inventories of carbon nanotubes (Singh et al., 2008), carbon nanofibers (Khanna et al., 2008), and nanoclays (Joshi, 2008) is evident. However, Singh et al. (2008) measured the water volume necessary during the production of carbon nanotubes using the processes CNT-PFR (0.108 L g^{-1}) and CNT-FBR (0.121 L g^{-1}). If these values are compared to the water volumes required only by Processes 1 (131 L g^{-1}) and 2 (138 L g^{-1}) in the EUC and EC systems,

Table 3
Life cycle inventory of EUC and EC systems to 1 g of nanowhiskers.

Substances	Compartments	Unit	EC	EUC	Occurrences of EC ≥ EUC in Monte Carlo uncertainty analysis, with 95% of confidence[a]
Energy, gross calorific value, in biomass	Raw material	kJ	136.03	801.50	0%
Energy, gross calorific value, in biomass, primary forest	Raw material	kJ	0.003	0.007	5%
Energy, kinetic (in wind), converted	Raw material	kJ	0.67	6.01	0%
Energy, potential (in hydropower reservoir), converted	Raw material	kJ	1663.52	15,136.18	0%
Energy, solar, converted	Raw material	kJ	0.01	0.05	0%
Total	Raw material	kJ	1800.23	15,943.75	
Water, cooling, unspecified natural origin/m^3	Raw material	L	0.94	4.20	0%
Water, lake	Raw material	L	0.001	0.008	0%
Water, river	Raw material	L	0.24	2.05	0%
Water, salt, ocean	Raw material	L	0.01	0.08	0%
Water, salt	Raw material	L	0.003	0.02	0%
Water, turbine use, unspecified natural origin	Raw material	L	3602.41	32,672.16	0%
Water, unspecified natural origin/m^3	Raw material	L	139.85	133.75	54%
Water, well, in ground	Raw material	L	2.87	0.11	100%
Total	Raw material	L	3746.32	32,812.38	
BOD_5, Biological Oxygen Demand	Water	g	0.11	3.12	0%
COD, Chemical Oxygen Demand	Water	g	0.37	6.35	0%
Furfural	Water	g	nd[b]	0.151	0%
HMF	Water	g	nd[b]	0.08	0%
Nitrate	Water	g	0.06	0.05	11%
Nitrogen	Water	g	0.0004	0.001	0%
Nitrogen, organic bound	Water	g	0.0003	0.002	0%
Nitrogen, total	Water	g	0.0001	0.009	0%
Total		g	0.001	0.01	
Phenol	Water	g	0.00004	0.10	0%
Phosphorus	Water	g	0.004	0.0007	100%
Phosphorus, total	Water	g	0.00001	0.004	0%
Total	Water	g	0.004	0.005	

[a] Monte Carlo uncertainty analysis, with 100 cycles.
[b] Not detected by the method. Source: Prepared by the authors.

respectively, then the production of cellulose nanowhiskers is also water intensive.

If the water volumes related only to cotton cultivation and to nanowhiskers extraction are considered, the perception that Processes 1 and 2 are significant water users is also clear. The volume of water required for the irrigation of cotton, used in the EC system (1.94 g of cotton), was 2 L, a relatively small amount when compared to that used by Process 2 (138 L) to produce 1 g of

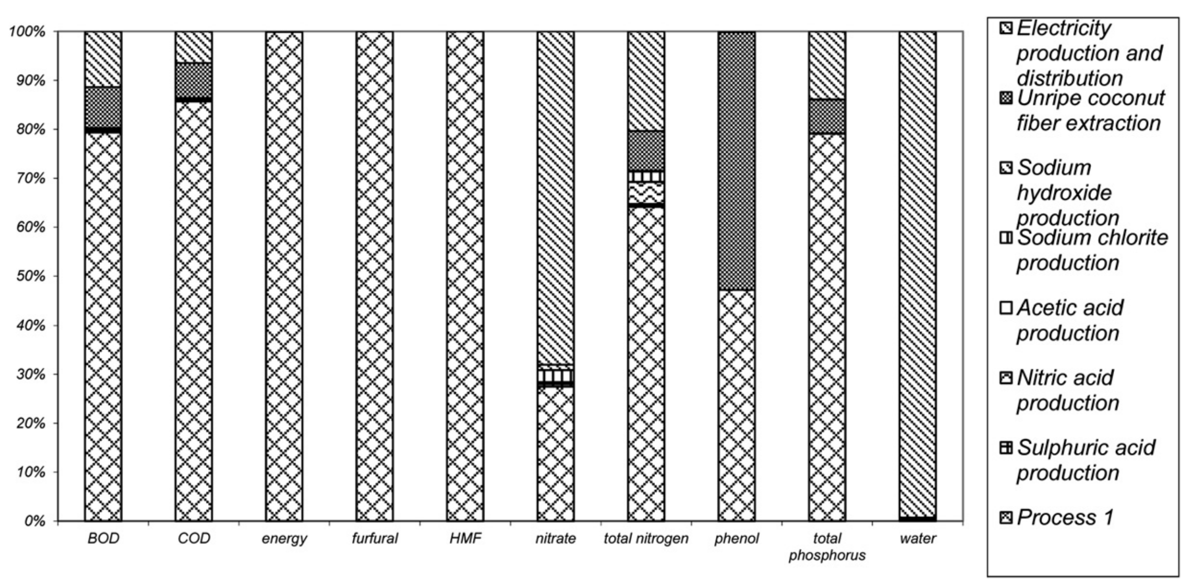

Fig. 3. Contribution of each process of the EUC system to the nanowhiskers life cycle inventory.

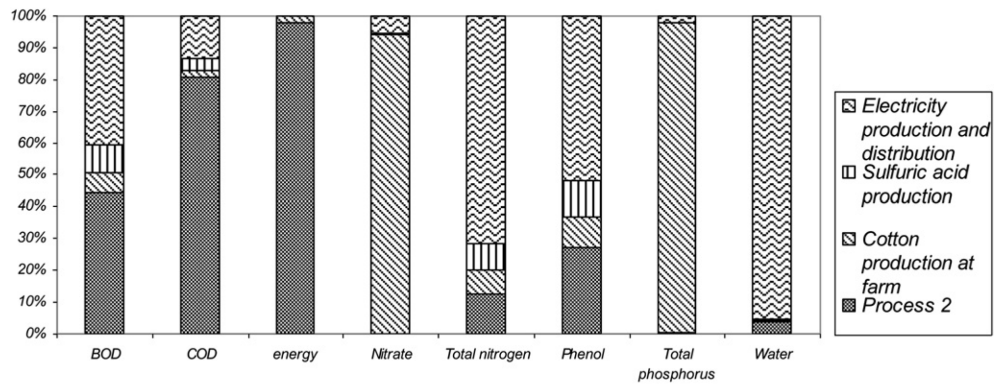

Fig. 4. Contribution of each process of the EC system to the nanowhiskers life cycle inventory.

nanowhiskers. As agricultural irrigation is the world's main user of water resources (WWAP, 2009), the volume used by Process 2 calls attention to the need to reduce water use in nanowhiskers extraction processes. In this light, Process 1 can also be classified as a water-intensive process because 131 L of water were used to produce 1 g of nanowhiskers.

4.1.3. Loads in liquid effluents

The EUC system generated effluents with significantly higher polluting loads in most of the analyzed substances (COD, BOD, total nitrogen, phenol, furfural, and HMF) than the EU system (Table 3). Although higher nitrate and total phosphorus loads occurred in effluents of the EC system, the differences between these systems were not significant.

Among the processes considered in the EUC system, the extraction of nanowhiskers (Process 1) is the main cause of the COD, BOD, total nitrogen, furfural, and HMF loads (Fig. 3). The phenol load came primarily from the extraction of unripe coconut fibers and from Process 1. The washing of fibers and the pre-treatments devoted to the removal of extractives and lignin in Process 1 release organic matter and nutrients that are primarily responsible for the COD, BOD, phenol, and total nitrogen loads.

The furfural and HMF loads were detected only in Process 1 of the EUC system, mainly when fiber hydrolysis was performed. According to Fengel and Wegener (2003), the production of furfural and HMF are related primarily to the dehydration of hemicellulose and cellulose at high temperature, especially when subject to acidic conditions. Although the hydrolysis temperature is the same in Processes 1 and 2, Process 1 uses higher sulfuric acid mass (Process 1: 64 percent w/w, Process 2: 60 percent w/w) and higher reaction time (Process 1: 120 min, Process 2: 70 min).

Considering the processes studied in the EU system, cotton production at farm is the main cause for the nitrate and total phosphorus loads (Fig. 4). The application of fertilizers in cotton fields results in the emission of these substances into water.

The life cycle inventory of nanoparticles, focusing on emissions into water, is rare in publicly available literature. Joshi (2008) presented the total COD, BOD, and nitrate loads generated in the cradle-to-gate study of nanoclays. According to this study, 0.00005 g of BOD, 0.0002 g of COD, and 0.00002 g of nitrate were emitted when 1 g of nanoclays was manufactured. These loads are much smaller than those generated by the EUC and EC systems (Table 3).

4.2. Life cycle impact assessment

The life cycle impact assessment of the EC and EUC systems shows that EUC can have a more significant impact on climate change, human toxicity, and eutrophication than EC (Table 4). While EUC may cause lower impact on water depletion in relation to EC, this difference was insignificant.

The production and distribution of electricity is the main process responsible for impacts on climate change, human toxicity, and eutrophication in both studied systems (Figs. 5 and 6). Because 87 percent of Brazilian electricity comes from hydroelectric power plants, according to the ecoinvent database (Dones et al., 2007), land transformation and the flooding of vegetation during reservoir construction and operation were responsible for the liberation of the higher amounts of carbon dioxide and methane that contribute to climate change.

On the other hand, the production of copper used in the cables that distribute electricity was the main process responsible for the emission of toxic substances and nutrients that lead to human toxicity as well as marine and freshwater eutrophication. In the EUC system, Process 1 also generated toxic substances and nutrients, as described in the inventory analysis, but the effect of these substances caused lower impacts in human toxicity and eutrophication than those substances released during the production and distribution of electricity. In the EC system, besides electricity production and distribution, the production of cotton on farms also significantly contributed to eutrophication.

Table 4
Results of impact categories for the EUC and EC systems to 1 g of nanowhiskers, according to ReCiPe (H).

Impact category	Unit	EC system	EUC system	Occurrences of EC $\geq$ EUC in Monte Carlo uncertainty analysis, with 95% of confidence
Climate change	kg CO_2 eq	0.122171	1.086412	0%
Human toxicity	kg 1,4-DB eq	0.034797	0.291122	0%
Freshwater eutrophication	kg P eq	0.000024	0.000134	0%
Marine eutrophication	kg N eq	0.000065	0.000320	0%
Water depletion	m^3	0.142959	0.135922	54%

Source: Prepared by the authors.

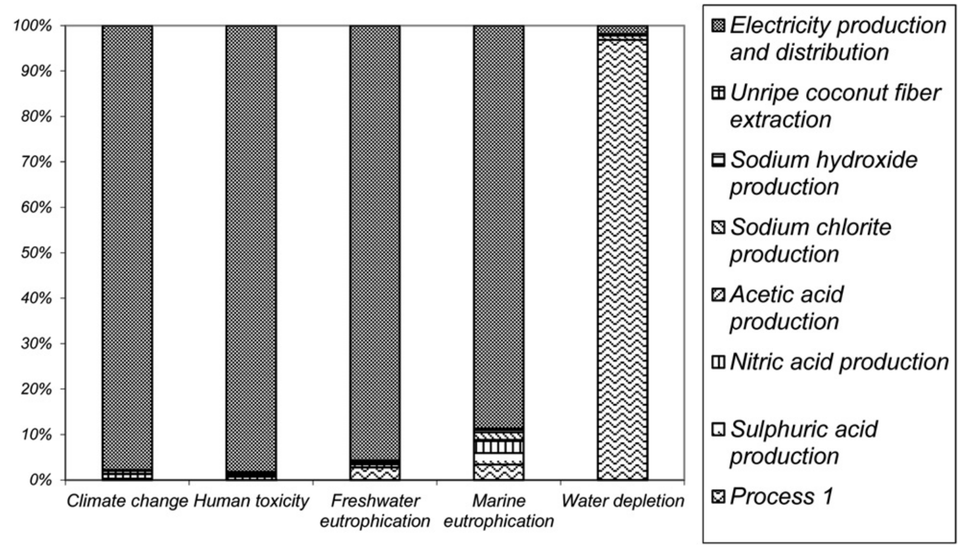

Fig. 5. Contribution of each process of the EUC system to the nanowhiskers life cycle impact assessment.

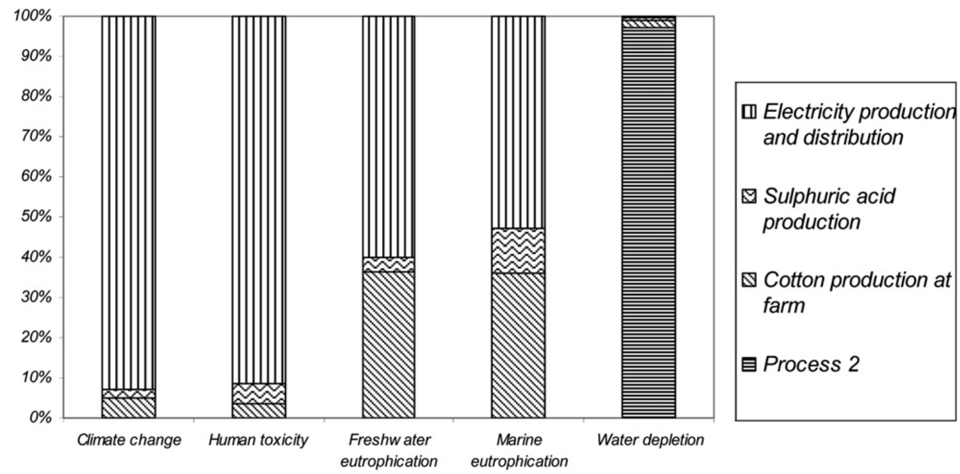

Fig. 6. Contribution of each process of the EC system to the nanowhiskers life cycle impact assessment.

Process 1, in the EUC system, and Process 2, in the EC system, were the main causes for the impact category regarding water depletion (Figs. 5 and 6). When water was analyzed in the inventory, the production and distribution of electricity was the main process using this resource. This difference in results occurs because the water depletion in ReCiPe accounts only for the following water categories, which lead to freshwater deviation from water bodies: water, lake; water, river; water, unspecified natural origin per cubic meter; and water, well, in ground (Goedkoop et al., 2009). In this sense, the main processes responsible for this impact category were Process 2, in the EC system, and Process 1, in the EC system. Water was mainly used to wash fibers, during pre-treatment stages in Process 1, and to correct the pH of nanowhiskers solutions, during dialysis in Processes 1 and 2.

The life cycle impact results obtained for cellulose nanowhiskers can also be compared to the results obtained for carbon nanofibers (Khanna et al., 2008), considering the categories of climate change and human toxicity that were measured in the same unit. According to Khanna et al. (2008), the production of 1 g of carbon nanofibers (using methane as feedstock) impacted climate change in the range of 0.7–1.3 kg of CO_2 equivalent and human toxicity in the range of 0.5–0.53 kg of 1.4-DB equivalent. The values of the impacts obtained for the EUC system (Table 4) were at the same level as these values, while those found for the EC system were lower.

5. Conclusions

The life cycle evaluation of cellulose nanowhiskers extracted from unripe coconut fibers (EUC system) and from white cotton fibers (EC system) showed that different fibers required different extraction processes resulting in the distinct generation of aspects and the level of environmental impacts. Nanowhiskers produced in the EC system required less energy and water, emitted less polluting loads, and contributed less to climate change, human toxicity, and eutrophication than those produced in the EUC system.

The extraction of nanowhiskers (Processes 1 and 2) was the main process responsible for critical energy use and impacts in both systems studied. Among all processes studied, Processes 1 and 2 required the most energy, which resulted in higher impacts on climate change, human toxicity, and eutrophication. These processes also used a considerable amount of freshwater, which contributed to water depletion.

Although the loads of COD, BOD, total nitrogen, furfural, and HMF from Process 1 were higher than the other loads from other processes of systems EUC and EC, they were not the main cause for the analyzed impacts. Substance loads emitted by electricity production and the distribution processes contributed most to these impacts.

When consumption (energy and water) and emissions (COD, BOD, and nitrate loads) of systems EC and EUC were compared to those related to the production of nanoclays, carbon nanotubes, and carbon nanofibers, the consumption and emission levels were also found to be high. The water volume required by EC and EUC systems was also perceived as elevated when compared to water used to irrigate cotton plants on farms. Reduction of water use is relevant, especially in semi-arid regions, such as in the Brazilian northeast, which struggles with low water availability even for drinking.

Cellulose nanowhiskers produced in the EUC system affected climate change and human toxicity at the same level as carbon nanofibers. From this perspective, nanowhiskers produced in the EC system performed better.

Therefore, before scaling up Processes 1 and 2, further research must seek alternatives to improve process yields and reduce energy and water use. The yield of Process 1 can be substantially improved with better control of fiber loss, especially during the chopping step. Modification of the hydrolysis step shall also be investigated in order to improve the yield in Processes 1 and 2.

Lower processing times and more energy efficient equipment, especially those responsible for heating chemical solutions, shall be researched to reduce the electricity demand in these processes. The reuse of water shall also be explored, considering water quality patterns at each phase of the nanowhisker extraction process. In process 1, the reuse of effluents from dialysis in the washing stage is being investigated. New technologies to produce nanowhiskers, such as enzymatic treatments (biobleaching), mechanical processes, ultrasonication, and green solvents, are alternatives that can also lead to higher environmental performance.

Another research theme to be pursued is the extraction of products (apart from cellulose nanowhiskers) from fibers rich in other substances, such as lignin and hemicellulose. The unripe coconut fiber is an example of a fiber with significant fractions of these substances. Extraction of other commercial materials reduces the overall impact associated with nanowhiskers when the allocation of inputs and outputs is performed. For instance, the lignin present in coconut fiber could be extracted and commercialized as bioadhesive. The way Process 1 was originally designed, lignin and hemicellulose are extracted but not recovered, which increases the polluting loads of the effluents released by this process.

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Appendix A. Processes used in the life cycle study of EC and EUC systems obtained from ecoinvent v2.

Process name in Figs. 1 and 2	Process name in the ecoinvent database (Jan/2011)
Electricity production and distribution	- Electricity, low voltage, production BR, at grid/BR U
Production of NaOH	- Sodium hydroxide, 50% in H_2O, production mix, at plant/RER U
Production of $NaClO_2$ [a]	- Hydrogen peroxide, 50% in H_2O, at plant/RER U - Sodium chlorate, powder, at plant/RER U - Sodium hydroxide, 50% in H_2O, production mix, at plant/RER U - Sulfuric acid, liquid, at plant/RER U
Production of H_2SO_4	- Sulfuric acid, liquid, at plant/RER U
Production of CH_3COOH	- Acetic acid, 98% in H_2O, at plant/RER U
Production of H_2NO_3	- Nitric acid, 50% in H_2O, at plant/RER U
Cotton production at farm	- Cotton fibers, at farm/US U

[a] Since the sodium chlorite production process does not exist in ecoinvent, the production process proposed by Ian et al. (2007) was used. Data related to energy and water use were not available for this process. According to Ian et al. (2007), the production of sodium chlorite requires sodium chlorate, hydrogen peroxide, sodium hydroxide, and sulfuric acid. The production process inventories of these chemicals were obtained from ecoinvent.

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